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# Nature of the local environment of germanium atoms in amorphous films $(\text{GeTe})_x(\text{Sb}_2\text{Te}_3)$

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Using Mossbauer spectroscopy on  $^{119}\text{Sn}$  impurity atoms, it was demonstrated that in amorphous  $(\text{GeTe})_x(\text{Sb}_2\text{Te}_3)$  films (where  $x = 0.5, 1, 2, 3$ ) tin atoms replace atoms of tetravalent germanium, which forms a tetrahedral system of chemical bonds with atoms in its local environment. In crystalline films, tin replaces divalent six-coordinated germanium in positions 4b of the NaCl-type crystal lattice.

**Keywords:** amorphous films, phase memory, Mossbauer spectroscopy.

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Phase memory materials based on chalcogenide alloys are used to store and encode data in non-volatile memory devices. The prerequisite for this is a noticeable difference in conductivity, as well as in the reflectivity of their crystalline and amorphous phases [1]. It is believed that alloys with compositions lying on the  $\text{GeTe}-\text{Sb}_2\text{Te}_3$  pseudobinary line are the most convenient materials for creating rewritable optical storage devices [2]. They have short crystallization times, ideal reversibility of transitions between amorphous and crystalline states, and high thermal stability. Obviously, to increase the recording density and to miniaturize memory devices, it is necessary to understand the details of the materials microstructure with a phase transition in both the crystalline and amorphous states.

At present, the crystal structures of  $(\text{GeTe})_x(\text{Sb}_2\text{Te}_3)$  alloys (where  $x = 0.5, 1, 2, 3$ ) are studied in details [3–6]. But, contradictions in the interpretation of experimental results obtained in the study of amorphous films  $\text{Ge}_2\text{Sb}_2\text{Te}_5$  by spectroscopy method of (extended X-ray absorption fine structure, EXAFS) [7–10]. This indicates the need to use other experimental methods more sensitive to minor changes in the local structure of the electron shells of atoms during the transition from amorphous to crystalline state. In particular, it was shown that Mossbauer spectroscopy is an effective tool for detecting changes in the local environment of atoms and their electronic structure during amorphization of compounds of type  $\text{Ge}_2\text{Sb}_2\text{Te}_5$  [11]. This paper relates to studying the nature of the local environment of germanium atoms in crystalline and amorphous films  $(\text{GeTe})_x(\text{Sb}_2\text{Te}_3)$  (where  $x = 0.5, 1, 2, 3$ ) by absorption Mossbauer spectroscopy on the isotope  $^{119}\text{Sn}$ .

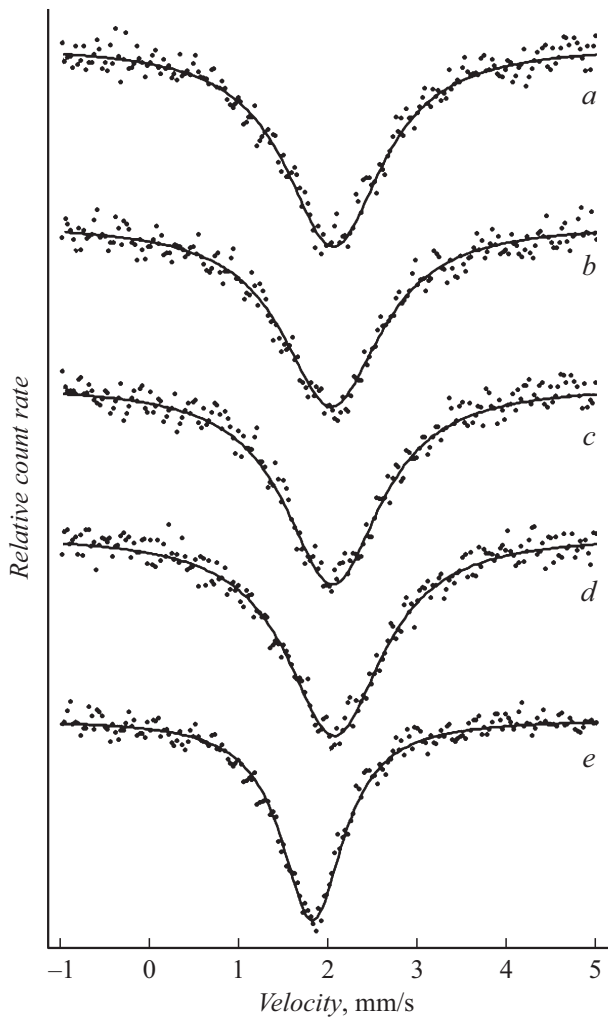
X-ray amorphous films  $a\text{-Ge}_3\text{Sb}_2\text{Te}_6$ ,  $a\text{-Ge}_2\text{Sb}_2\text{Te}_5$ ,  $a\text{-GeSb}_2\text{Te}_4$ ,  $a\text{-GeSb}_4\text{Te}_7$  (denoted as  $a\text{-GeSbTe}$ ) and  $a\text{-Ge}_{2.95}\text{Sn}_{0.05}\text{Sb}_2\text{Te}_6$ ,  $a\text{-Ge}_{1.95}\text{Sn}_{0.05}\text{Sb}_2\text{Te}_5$ ,

$a\text{-Ge}_{0.95}\text{Sn}_{0.05}\text{Sb}_2\text{Te}_4$  and  $a\text{-Ge}_{0.95}\text{Sn}_{0.05}\text{Sb}_4\text{Te}_7$  (let's denote them as  $a\text{-Ge}(\text{Sn})\text{SbTe}$ ) were obtained by magnetron sputtering of polycrystalline targets of the same composition at direct current in a nitrogen atmosphere on aluminum foil substrates. Then the films were annealed at temperatures of 150–200°C to obtain  $c\text{-Ge}_3\text{Sb}_2\text{Te}_6$ ,  $c\text{-Ge}_2\text{Sb}_2\text{Te}_5$ ,  $c\text{-GeSb}_2\text{Te}_4$ ,  $c\text{-GeSb}_4\text{Te}_7$  (denoted as  $c\text{-GeSbTe}$ ) and  $c\text{-Ge}_{2.95}\text{Sn}_{0.05}\text{Sb}_2\text{Te}_6$ ,  $c\text{-Ge}_{1.95}\text{Sn}_{0.05}\text{Sb}_2\text{Te}_5$ ,  $c\text{-Ge}_{0.95}\text{Sn}_{0.05}\text{Sb}_2\text{Te}_4$  and  $c\text{-Ge}_{0.95}\text{Sn}_{0.05}\text{Sb}_4\text{Te}_7$  (we denote them as  $c\text{-Ge}(\text{Sn})\text{SbTe}$ ). The described compositions are given for sputtered targets. The thickness of the films was determined using an atomic force microscope and ranged from 40 to 120 μm. For the synthesis of tin-containing alloys, the  $^{119}\text{Sn}$  isotope of 96

Germanium doped with tin was obtained by sputtering a film of metallic tin (enriched to 96

The Mossbauer spectra of  $^{119}\text{Sn}$  were recorded on a SM 4201 TerLab spectrometer at 80 K with a  $\text{Ca}^{119\text{mm}}\text{SnO}_3$  source. The instrumental spectral linewidth ( $G_{app}$ ) for the  $^{119}\text{Sn}$  isotope was 0.79(2) mm/s. Isomeric shifts  $\delta$  of  $^{119}\text{Sn}$  spectra are given relative to the  $\text{CaSnO}_3$  absorber. The Mossbauer spectra of  $^{119}\text{Sn}$  atoms in the  $a\text{-Ge}(\text{Sn})\text{SbTe}$  and  $c\text{-Ge}(\text{Sn})\text{SbTe}$  films are shown in Figs 1 and 2. In interpreting the Mossbauer spectroscopy data, it was assumed that the impurity tin atoms isovalently substitute for germanium atoms in amorphous and crystalline films.

The Mossbauer spectra of all  $a\text{-Ge}(\text{Sn})\text{Sb}$  films are single broadened lines ( $G \sim 1.33\text{--}1.36$  mm/s) with isomeric shifts  $\delta \sim 2.04\text{--}2.07$  mm/s. These shifts are close to the isomeric shifts of the spectra of impurity tin atoms in crystalline germanium (Fig. 1), as well as to the isomeric shift of the  $\alpha\text{-Sn}$  gray tin spectrum. The isomeric shifts of these two spectra ( $\delta = 1.79$  mm/s for Ge and  $\delta = 2.10$  mm/s for  $\alpha\text{-Sn}$ ) form the region of isomeric shifts



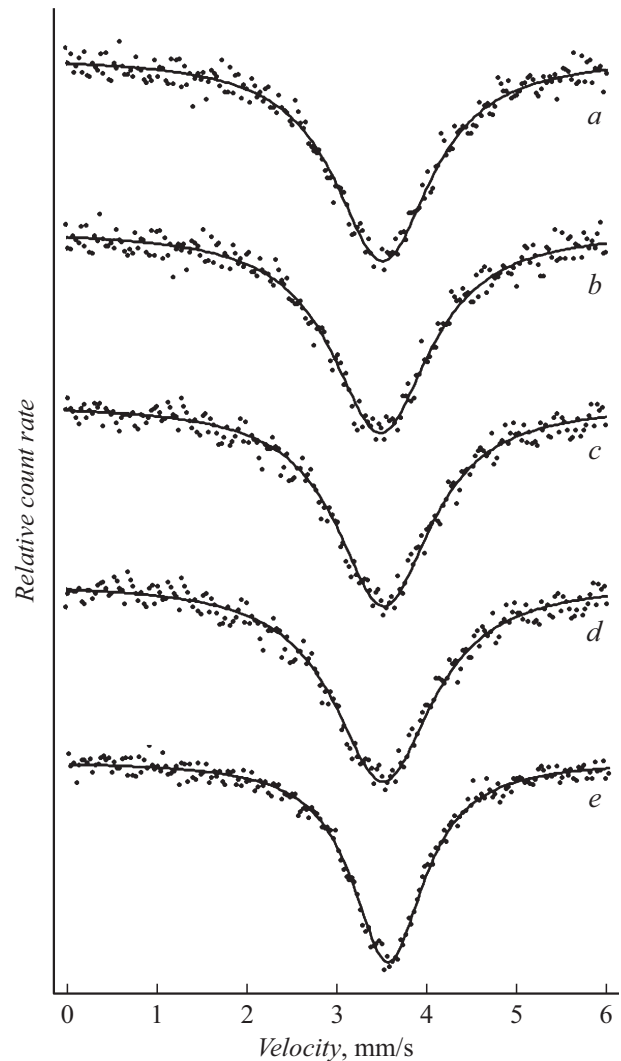
**Figure 1.** Messbauer spectra  $^{119}\text{Sn}$  of  $a\text{-Ge}_{2.95}\text{Sn}_{0.05}\text{Sb}_2\text{Te}_6$  (a),  $a\text{-Ge}_{1.95}\text{Sn}_{0.05}\text{Sb}_2\text{Te}_5$  (b),  $a\text{-Ge}_{0.95}\text{Sn}_{0.05}\text{Sb}_2\text{Te}_4$  (c),  $a\text{-Ge}_{0.95}\text{Sn}_{0.05}\text{Sb}_4\text{Te}_7$  (d) and crystalline germanium (e).

of tetravalent tin compounds with tetrahedral  $sp^3$ -system of chemical bonds. Hence, impurity tin atoms in the structure of  $a\text{-Ge}(\text{Sn})\text{Sb}$  films isovalently replace the fourvalent germanium atoms, which form a tetrahedral chemical bond, i.e., local coordination number of germanium atoms in amorphous films is four).

Note that if in the  $a\text{-Ge}(\text{Sn})\text{SbTe}$  films in the local environment of germanium atoms (and tin atoms replacing them) there are only germanium atoms, then the isomeric shift of the spectra  $^{119}\text{Sn}$  of the films should be  $\sim 1.8$  mm/s (as in the spectrum of impurity atoms  $^{119}\text{Sn}$  in germanium). If in the  $a\text{-Ge}(\text{Sn})\text{SbTe}$  films in the local environment of germanium atoms (and tin atoms replacing them) there are only tellurium atoms, then the isomeric shift of the spectra  $^{119}\text{Sn}$  of the films should be  $\sim 2.1$  mm/s (as in the  $^{119}\text{Sn}$  spectrum of  $\text{Ge}_{1.45}\text{Sn}_{0.05}\text{Te}_{8.5}$  glassy alloys [12]). Based on this, it should be concluded that the  $^{119}\text{Sn}$  Messbauer spectra of the  $a\text{-Ge}(\text{Sn})\text{SbTe}$  films correspond to germanium atoms (and tin atoms

replacing them), in the local environment of which there are germanium atoms, and predominantly tellurium atoms.

Kolobov et al. [7] to interpret the EXAFS data obtained in the study of the order–disorder transition in  $\text{Ge}_2\text{Sb}_2\text{Te}_5$  suggested the model of „umbrella flip“. According to this model, film amorphization is accompanied by a jump of the Ge atom from the octahedral position occupied in the crystalline film to the tetrahedral position surrounded by four tellurium atoms, and Ge–Ge bonds were not found. However, Baker et al. [8,9], also using EXAFS data to study films  $a\text{-Ge}_2\text{Sb}_2\text{Te}_5$ , propose a model according to which germanium atoms form the structural units  $\text{Te}_3\text{Ge}\text{--GeTe}_3$ , and the model is based on the predominant formation of bonds in amorphous films Ge–Ge. Finally, the structure of  $a\text{-Ge}_2\text{Sb}_2\text{Te}_5$  and  $a\text{-GeSb}_2\text{Te}_4$  films was examined by the authors [10] by the EXAFS method also. It was shown that Ge–Ge and Ge–Sb bonds are present in crystalline and amorphous films, while Te–Te and Sb–Sb bonds were not



**Figure 2.** Messbauer spectra  $^{119}\text{Sn}$  of  $c\text{-Ge}_{2.95}\text{Sn}_{0.05}\text{Sb}_2\text{Te}_6$  films (a),  $c\text{-Ge}_{1.95}\text{Sn}_{0.05}\text{Sb}_2\text{Te}_5$  (b),  $c\text{-Ge}_{0.95}\text{Sn}_{0.05}\text{Sb}_2\text{Te}_4$  (c),  $a\text{-Ge}_{0.95}\text{Sn}_{0.05}\text{Sb}_4\text{Te}_7$  (d) and  $\text{SnTe}$  (e) compounds.

found. All atoms satisfy the formal valence requirements, and the germanium atoms have quadruple coordination.

The Messbauer spectroscopy data obtained allow us to conclude that tetravalent germanium atoms form a tetrahedral  $sp^3$  system of chemical bonds in the structural grid of the amorphous matrix (local coordination number of germanium atoms is four) and have mainly tellurium atoms in their closest environment (although germanium atoms are not excluded).

A characteristic feature of the spectra of impurity tin atoms in amorphous films is their broadening, and two reasons for this broadening can be proposed. The first reason is that possible distortions of the angles between the bonds of tin atoms with tellurium atoms in its nearest environment lead to spectrum broadening due to the unresolved quadrupole splitting  $QS \sim 0.55$  mm/s, which indicates a significant distortion tetrahedral bond angles. The second reason for the spectra broadening is fluctuations in the distances from tin atoms to tellurium atoms, while maintaining the tetrahedral system of chemical bonds. This leads to spectrum broadening due to the heterogeneous isomeric shift. Using the calibration of the isomeric shifts of the  $^{119}\text{Sn}$  Messbauer spectra given in [13], we found that the electronic configurations of tin lie within  $5s^{0.92}p^{2.76}$  to  $5s^{1.15}p^{3.45}$ , and the most probable configuration  $5s^{1.01}p^{3.03}$  corresponds to the atomic configuration when four atoms of tellurium are at equal distances in the nearest environment of tin atoms.

The Messbauer spectra  $^{119}\text{Sn}$  of all  $c\text{-Ge}(\text{Sn})\text{Sb}$  films are single broadened lines ( $G \sim 1.30\text{--}1.35$  mm/s) with isomeric shifts within  $\delta \sim 3.49\text{--}3.51$  mm/s. So, spectra of  $c\text{-Ge}(\text{Sn})\text{SbTe}$  films have isomeric shifts typical of the spectra of  $^{119}\text{Sn}$  ion compounds of divalent tin. For understanding, Fig. 2 shows the spectrum of the divalent tin compound  $\text{SnTe}$ , for which  $\delta = 3.54$  mm/s.

$c\text{-GeSbTe}$  compounds have three crystalline phases: a metastable vacancy-disordered cubic phase (can be obtained by heating an amorphous sample above the crystallization temperature of  $150^\circ\text{C}$ ), a vacancy-ordered cubic phase (can be obtained by annealing amorphous samples at  $300^\circ\text{C}$ ) and the hexagonal phase (obtained by prolonged heating of an amorphous sample at a temperature above  $300^\circ\text{C}$ ) [3,4]. The general structure of these compounds consists of rock salt-type construction blocks with alternating cationic ( $\text{GeSb}$ ) and anionic ( $\text{Te}$ ) layers [3,4].

The Messbauer spectroscopy data on  $^{119}\text{Sn}$  impurity atoms are consistent with the results of X-ray diffraction studies of  $c\text{-GeSbTe}$  [3,4] crystalline compounds: bivalent tin  $\text{Sn}^{2+}$  (electronic configuration  $5s^2p^x$ ) replaces divalent germanium  $\text{Ge}^{2+}$  (electronic configuration  $4s^2p^x$ ) in positions  $4b$  crystal lattice like  $\text{NaCl}$ . The isomeric shifts of the spectra of these compounds are close to the isomeric shift of the  $\text{SnTe}$  compound, which also has a crystal lattice of the  $\text{NaCl}$  type. The spectra broadening of ternary compounds (compared to the spectral width of  $\text{SnTe}$   $G = 0.94$  mm/s) is due to the presence of a

high concentration of stoichiometric vacancies [3,4] in the cationic sublattice of these compounds.

Thus, the germanium atoms in the structure of the  $a\text{-GeSbTe}$  films are tetravalent, form a tetrahedral system of chemical bonds (the local coordination number of germanium atoms is four), and tellurium atoms are predominantly located in the local environment of germanium atoms. The Messbauer spectroscopy data on  $^{119}\text{Sn}$  impurity atoms for  $c\text{-GeSbTe}$  films correspond to divalent tin replacing divalent germanium in the crystal lattice of the  $\text{NaCl}$  type.

## Conflict of interest

The authors declare that they have no conflict of interest.

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