

A. B. Zayceva, A. B. Nikolaeva, A. B. Marchenko

ЛОКАЛЬНАЯ СИММЕТРИЯ И ЭЛЕКТРОННАЯ СТРУКТУРА АТОМОВ РЕШЕТОК $Pb_{1-x}Sn_xTe$ В ОБЛАСТИ БЕСЩЕЛЕВОГО СОСТОЯНИЯ

Методом мессбауэровской спектроскопии на изотопах $^{67}Ga(^{67}Zn)$, ^{119}Sn и $^{129m}Te(^{129}I)$ показано, что для твердых растворов $Pb_{1-x}Sn_xTe$ в области существования бесщелевого состояния как при 80, так и при 295 K не наблюдаются изменения локальной симметрии узлов, электронной структуры атомов и интенсивности электрон-фононного взаимодействия.

Ключевые слова: мессбауэровская спектроскопия, локальная симметрия, бесщелевое состояние.

A. Zaiceva, A. Nikolaeva, A. Marchenko

Local Symmetry and Electron Structure of Atoms in the $Pb_{1-x}Sn_xTe$ Lattices Within the Gapless State Range

The Mössbauer spectroscopy with the $^{67}Ga(^{67}Zn)$, ^{119}Sn and $^{129m}Te(^{129}I)$ isotopes has shown that no modifications of lattice sites local symmetry, electron structure of atoms and intensity of electron-phonon interaction are revealed for the $Pb_{1-x}Sn_xTe$ solid solutions in the range of gapless state at both 80 and 295 K.

Keywords: Mossbauer spectroscopy, local symmetry, gapless state.

1. Introduction

In the $Pb_{1-x}Sn_xTe$ system there are continuous solid solutions with the NaCl-type lattice. Inversion of zones with gapless state is observed in these solid solutions at $x = 0.62$ and $x = 0.40$ at 295 and 80 K, respectively [1]. To find possible modifications of a local symmetry for cation and anion sites, of electron structure for the lattice atoms as well as of electron-phonon interaction in the gapless state range we have investigated the $Pb_{1-x}Sn_xTe$ solid solutions ($0 \leq x \leq 1$) by the Mössbauer spectroscopy using the ^{119}Sn (absorption spectroscopy), $^{67}Ga(^{67}Zn)$ and $^{129m}Te(^{129}I)$ (emission spectroscopy) isotopes.

2. Experimental details

The $Pb_{1-x}Sn_xTe$ solid solutions were synthesized by alloying starting components of semiconductor purity in quartz ampoules evacuated up to 10^{-2} mm Hg with following annealing of ingots and then of compressed powders at 650 °C for 120 hours. The quantities of components took into account that a homogeneity range is shifted to Te for the solid solutions enriched by tin telluride (about 50.1 at.% Te [1]). The X-ray analysis evidenced for homogeneity and the NaCl-type structure of all samples under investigation. For lead telluride enriched alloys, a linear dependence of the lattice constant on the solid solution composition was revealed whereas a devia-

tion from the linearity was observed at $x > 0.7$. All samples were of p-type conductivity and their hole concentration at 80 K varied from 10^{17} sm^{-3} for PbTe to 10^{21} sm^{-3} for SnTe.

Samples for the ^{119}Sn Mössbauer studies were prepared using tin enriched by the ^{119}Sn isotope up to 96%. Samples (sources) for the ^{67}Ga (^{67}Zn), $^{129\text{m}}\text{Te}$ (^{129}I) Mössbauer investigations were synthesized with a ^{67}Ga and $^{129\text{m}}\text{Te}$ radioactive preparations.

The ^{119}Sn and $^{129\text{m}}\text{Te}$ (^{129}I) Mössbauer spectra were recorded using a commercial spectrometer MS-2201 with following computer treatment. The ^{119}Sn spectra were recorded at 80 and 295 K whereas the $^{129\text{m}}\text{Te}$ (^{129}I) spectra at 80 K only. The ^{67}Zn Mössbauer spectra were recorded in conventional transmission geometry using the modified commercial spectrometer MS-2201. The electrodynamic driver of the spectrometer was replaced by a piezoelectric one on the basis of the PZT ceramics. A piezoceramic cylinder was set up within a cylindrical Perspex unit and caused a motion of an aluminum container with a ^{67}ZnS absorber at 4.2 K (the surface density of 1 g/sm^2 relative to ^{67}Zn). The sources were fixed at the opposite end of the Perspex unit. A motion was produced by an integrated and amplified low frequency drive signal of the basic spectrometer. The drive system did not include feedback. The velocity range $\pm 150 \text{ }\mu\text{m/s}$ was scanned.

A $\text{Ca}^{119\text{mm}}\text{SnO}_3$ source was applied at measurements of the ^{119}Sn Mössbauer spectra. A determination of the Mössbauer factor f was carried out using a relation [2]:

$$G_{\text{exp}} = G_a + G_s + 0.27G_{\text{nat}}t \quad (1)$$

where $t = n\sigma_0f$, n is the surface density of absorber relative to the ^{119}Sn isotope (in at/cm^2), $\sigma_0 = 1.4 \cdot 10^{-18} \text{ sm}^2$ is the maximum value of the resonance absorption cross-section, G_{exp} is the experimental spectral line width, G_a and G_s are the line widths of an absorber and the source, respectively, $G_{\text{nat}} = 0.3235 \text{ mm/s}$ is the natural line width for ^{119}Sn . The measurements were carried out with a set of absorbers having surface densities from 0.02 up to 2.0 mg/sm^2 relative to ^{119}Sn . Eq. (1) is valid for $(G_{\text{nat}}/G_a)t < 5$ and this condition is satisfied for all the solid solutions investigated and all the absorbers used. It is essential that the described method to determine f does not require a registration of the background gamma count rate. An extrapolation of straight lines (1) to $t = 0$ allows to find the experimental line width of extremely thin absorber G_0 . The G_0 dependence on solid solution composition is more interesting than the similar G_{exp} dependence because the last value is sensitive to an absorber surface density. For example, increasing temperature from 295 to 80 K resulted in increasing G_{exp} value from 0.98 up to 1.40 mm/s for a SnTe absorber with the 1 mg/sm^2 density ($n = 5 \cdot 10^{18} \text{ at/sm}^2$).

While investigating the $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$ solid solutions by the $^{129\text{m}}\text{Te}$ (^{129}I) emission Mössbauer spectroscopy, measurements of areas S under normalized Mössbauer spectra were carried out. The spectra had been recorded using a K^{129}I absorber with the surface density 15 mg/sm^2 relative to ^{129}I . Along with the 27.77 keV line corresponding to a transition of ^{129}I from the first excited state to the ground one, a gamma-spectrum of a $^{129\text{m}}\text{Te}$ source also contains K_α and K_β — lines of X-ray radiation arising due to the internal conversion of the 106 keV isomer transition in the $^{129\text{m}}\text{Te}$ nuclei. The energies of the $K_{\alpha 2}$, $K_{\alpha 1}$, $K_{\beta 3}$ and $K_{\beta 1}$ -lines are equal to 27.1, 27.5, 30.9 and 31.0 keV, respectively. Thus tin is a critical filter relative to K_β radiation of Te because a binding energy of tin K-electrons is 29.2 keV. Therefore a fraction of the 27.77 keV Mössbauer quanta in total radiation and a relative area of the Mössbauer spectrum should strongly depend on a tin amount in a source. For this reason a ratio of the lead, tin and tellurium amounts in all sources was kept constant at the S measurement by adding necessary portions of nonradioactive PbTe or SnTe providing identical X-ray absorption in the sources. Under these conditions, a ratio of the areas under the normalized spectra of two solid solutions can be considered as a ratio of their

Mössbauer factors. To find line width of the extremely thin absorber, the $^{129m}Te(^{129}I)$ Mössbauer spectra of $Pb_{1-x}Sn_xTe$ solid solutions were also measured with $K^{129}I$ absorbers of various surface densities (from 1.5 up to 15 mg/sm^2 relative to ^{129}I).

3. Experimental results and discussion

The ^{119}Sn and $^{129m}Te(^{129}I)$ Mössbauer spectra of all $Pb_{1-x}Sn_xTe$ samples were single lines (Fig. 1) with line widths G_0 close to the double natural width $2G_{nat}$ and insignificantly increasing with the increase of x . The dependence $G(x)$ is described by the expressions: G (mm/s) = 1.24 + 0.18 x for spectra ^{129}I at 80 K, G (mm/s) = 1.21 + 0.2 x for spectra ^{119}Sn at 80 K and G (mm/s) = 1.20 + 0.18 x for spectra ^{119}Sn at 295 K.

Maximum G_0 values are revealed for SnTe (Fig. 2). This is not unexpected because the homogeneity range increase in the solid solutions with the increase of tin content that results in higher defect concentration and broadening of the Mössbauer spectra. No anomalous variations of line width are found near the gapless state of the solid solutions at both 80 and 295 K (Fig. 2). It is possible, therefore, to draw a conclusion that a local symmetry of both cation and anion sites of the $Pb_{1-x}Sn_xTe$ lattices is unchanged over the whole range of the solid solutions existence.

Fig. 1. Mössbauer spectra of $^{129}Te(^{129}I)$ and ^{119}Sn measured on a $Pb_{0.6}Sn_{0.4}Te$ solid solution at 80 K

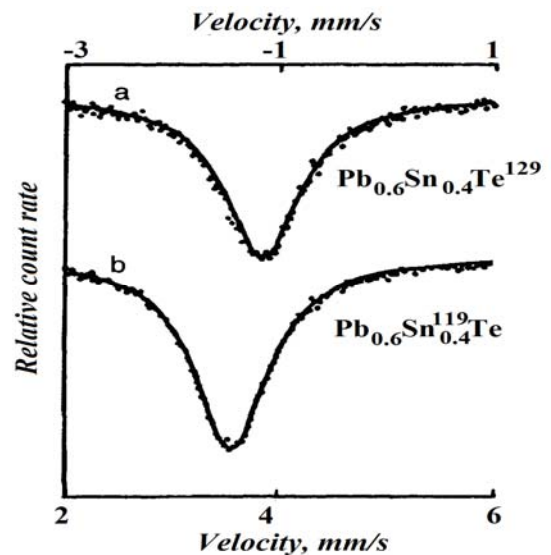
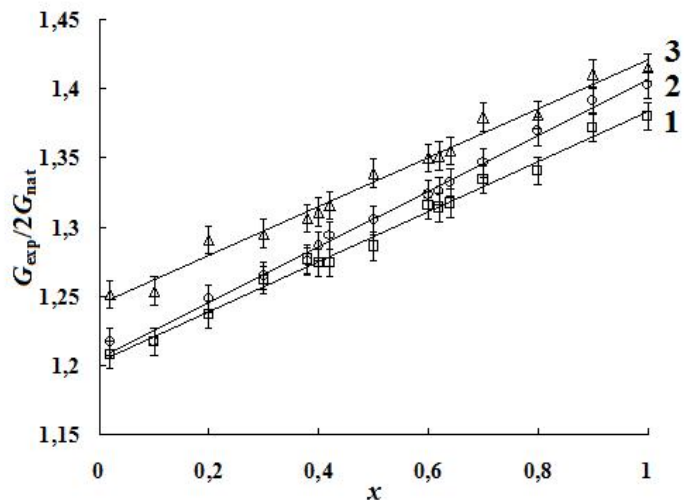


Fig. 2. The dependencies of experimental line widths G_{exp} (given in units of the double natural width $2G_{nat}$) on the composition of the $Pb_{1-x}Sn_xTe$ solid solutions: 1 — data for ^{119}Sn at 295 K, 2 — data for ^{119}Sn at 80 K, 3 — data for $^{129m}Te(^{129}I)$ at 80 K.

The dotted lines indicate the compositions with the gapless state at 80 and 295 K



The isomer shift of Mössbauer spectra is determined by chemical nature of atoms in a local environment of a Mössbauer probe. As a variation of composition of the $Pb_{1-x}Sn_xTe$ solid solutions does not change the nearest environment of tin atoms (6 Te atoms in the regular octahedron vertices), the isomer shift of the ^{119}Sn spectra was expected to be constant for all solid solutions. Measurements revealed it coinciding with the SnTe isomer shift within the error limit (Fig. 3).

For the $^{129m}Te(^{129}I)$ Mössbauer probe, a gradual substitution of lead atoms by tin ones occurs in local environment of ^{129m}Te (and, therefore, of the daughter ^{129}I atom) with the increase of x . The dependence $IS(x)$ is described by the expression $IS(mm/s) = 0.19x$. This effect should lower an ionicity of chemical bonds of iodine atoms and, as a result, rise the ^{129}I isomer shift. As it is seen from Fig. 3, this increase is revealed in the $^{129m}Te(^{129}I)$ emission Mössbauer spectra at a transition from PbTe to SnTe. The isomer shift values correspond to monovalent iodine Γ . Like for the ^{119}Sn spectra, no anomalous variations in the $^{129m}Te(^{129}I)$ spectra are found near the gapless state of the solid solutions.

A gradual rise of the Mössbauer factors f both for cation and anion sites is observed at a transition from PbTe to SnTe (see Fig. 4). The dependences $f(x)$ are described by the expressions: $f = 0.80 + 0.20x$ for spectra ^{129}I at 80 K, $f = 0.84 + 0.16x$ for spectra ^{119}Sn at 80 K and $f = 0.74 + 0.26x$ for spectra ^{119}Sn at 295 K. Such behavior of f can be clearly explained by close values of the Debye temperatures (125 K for PbTe and 130 K for SnTe) and considerable difference between tin and lead masses. It is essentially that no anomalies are observed in the $f(x)$ dependencies near the gapless state.

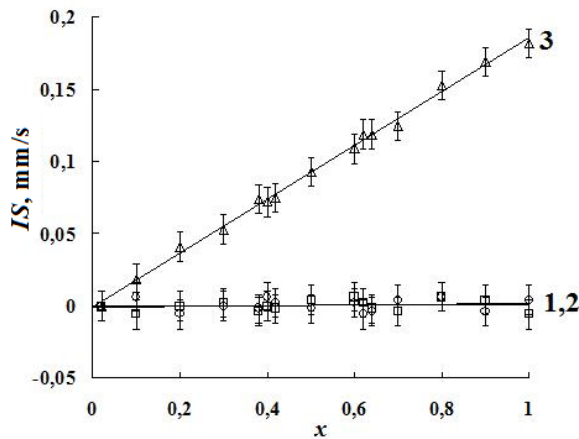


Fig. 3. The dependencies of the isomer shift IS (relative to PbTe at corresponding temperatures) on the composition of the $Pb_{1-x}Sn_xTe$ solid solutions: 1 — data for ^{119}Sn at 295 K, 2 — data for ^{119}Sn at 80 K, 3 — data for $^{129m}Te(^{129}I)$ at 80 K. The dotted lines indicate the compositions with the gapless state at 80 and 295 K

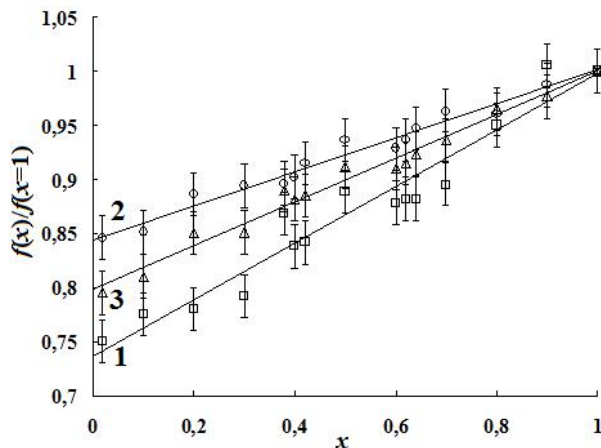


Fig. 4. The dependencies of the relative Mössbauer factors $f(x)/f(x=1)$ on the composition of the $Pb_{1-x}Sn_xTe$ solid solutions: 1 — data for ^{119}Sn at 295 K, 2 — data for ^{119}Sn at 80 K, 3 — data for $^{129m}Te(^{129}I)$ at 80 K. The dotted lines indicate the compositions with the gapless state at 80 and 295 K

In the first place we determined the position of the Zn impurity atoms in lead chalcogenide lattices (PbS, PbSe, and PbTe) using emission Mössbauer spectroscopy of $^{67}\text{Cu}(^{67}\text{Zn})$ and $^{67}\text{Ga}(^{67}\text{Zn})$ isotopes. The samples of PbS, PbSe, and PbTe were either of the n -type (with excess of Pb; the electron concentration $n \sim 10^{18} \text{ cm}^{-3}$) or of the p -type (with excess of chalcogen; the hole concentration $p \sim 10^{18} \text{ cm}^{-3}$), while the $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$ solid solutions were of the p -type (the hole concentration varied from 10^{17} cm^{-3} in PbTe to 10^{21} cm^{-3} in SnTe at $T = 80 \text{ K}$). We prepared the Mössbauer sources through diffusion doping of the samples with radioactive ^{67}Ga and ^{67}Cu isotopes in evacuated quartz cells at $T = 650 \text{ }^\circ\text{C}$ for 2h; the concentration of the parent isotope did not exceed $5 \cdot 10^{15} \text{ cm}^{-3}$. Typical $^{67}\text{Ga}(^{67}\text{Zn})$ and $^{67}\text{Cu}(^{67}\text{Zn})$ Mössbauer spectra for PbS are shown in Fig. 5.

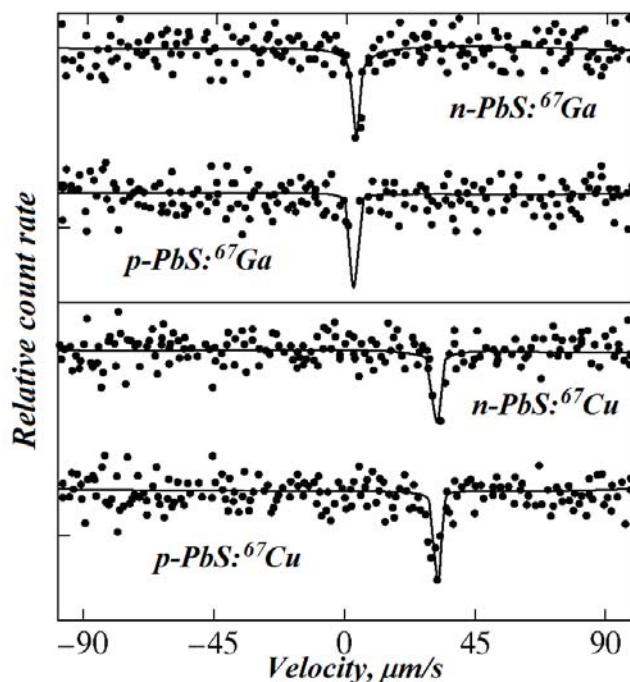


Fig. 5. Emission Mössbauer spectra of the impurity atoms: $^{67}\text{Ga}(^{67}\text{Zn})$ and $^{67}\text{Cu}(^{67}\text{Zn})$ in n -PbS and p -PbS at $T = 4.2 \text{ K}$

The spectra of $^{67}\text{Ga}(^{67}\text{Zn})$ for the lead chalcogenide consist of single lines with a width at half-height which is close to the instrumental resolution ($2.6 \pm 0.3 \text{ } \mu\text{m/s}$). The isomeric shift of these lines increases in the following series of compounds: PbS ($IS = 2.2 \pm 0.4 \text{ } \mu\text{m/s}$), \rightarrow PbSe ($IS = 10.3 \pm 0.4 \text{ } \mu\text{m/s}$), \rightarrow PbTe ($IS = 33.7 \pm 0.3 \text{ } \mu\text{m/s}$). The spectra are related to isolated impurity centers of Zn at the lead sites. The increase in the isomeric shift in the above-mentioned series is caused by variation in the ionicity of the chemical bond between the zinc atoms and the atoms in its first coordination sphere. The isomeric shift of the spectra is almost independent of the type of sample conductivity, and, therefore, the impurity center of Zn is either electrically inactive or recharging the shallow center does not affect the isomeric shift.

The spectra of $^{67}\text{Cu}(^{67}\text{Zn})$ for lead chalcogenides also consist of single lines with the width at half-height close to the instrumental resolution. Their isomeric shift is appreciably displaced to the metallic Zn spectrum: $IS = 31.1 \pm 0.4 \text{ } \mu\text{m/s}$ for PbS, $IS = 32.5 \pm 0.4 \text{ } \mu\text{m/s}$ for PbSe, and $IS = 41.2 \pm 0.4 \text{ } \mu\text{m/s}$ for PbTe. The spectra correspond to isolated Zn centers that formed as a result of

the radioactive decay of the interstitial parent Cu atoms in the lead chalcogenide lattices. At the same time, lead and chalcogen atoms occur as the nearest neighbors of the interstitial impurity atoms of Zn. Since the isomeric shift of the spectra is independent of the type of sample conductivity, we may conclude that, in this case, the Zn centers are also electrically inactive.

The Mössbauer spectra of $^{67}\text{Ga}(^{67}\text{Zn})$ for the $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$ solid solutions consist of single lines which are related to the Zn atoms at the sites of the cation sublattice. The line width in all spectra is close to the instrumental resolution. It slightly increases with x , approaching the maximum value for SnTe (the dependence $G(x)$ is described by the expression: $G(\mu\text{m/s}) = 0.08 + 5.17x$) (Fig. 6). This fact is quite expected since the homogeneity region expands as the Sn content increases in the alloy. This causes an increase in the concentration of structural point defects and, as a result, an increase in the width of the Mössbauer spectrum. A similar effect was also observed for the Mössbauer spectrum of ^{119}Sn and ^{129}Te (^{129}I) in the $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$ solid solutions.

The isomeric shift of the Mössbauer spectra is governed by the chemical nature of atoms in the local environment of the Mössbauer probe. Since the variation in composition of the $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$ solid solution does not affect the symmetry of the local environment of zinc atoms (tin atoms only substitute lead atoms in the second coordination shell), a weak dependence of the isomeric shift of the $^{67}\text{Ga}(^{67}\text{Zn})$ Mössbauer spectra on the composition (Fig. 6) is quite expected (The dependence $IS(x)$ is described by the expression $IS(\mu\text{m/s}) = 0.80 + 0.20x$).

It is essential that anomalous changes in both the isomeric shift and the spectrum width in the zero-gap state do not occur. In other words, we did not observe variation in the local symmetry of the cation sites and in the corresponding electron density in zero-gap $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$ solid solutions at $T = 80$ K.

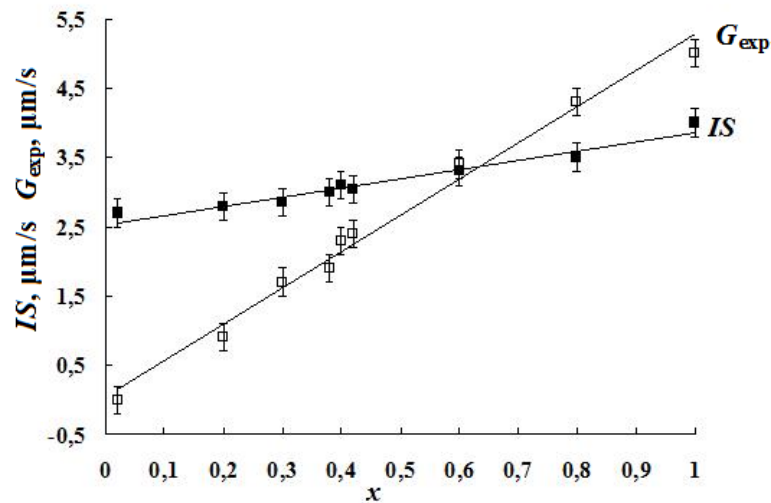


Fig. 6. The dependencies of the isomer shift IS (relative to $\text{PbTe}:^{67}\text{Ga}$) and of experimental line widths G_{exp} on the composition of the $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$ solid solutions at 80 K. The dotted line indicate the composition with the gapless state at 80 K

4. Conclusion

Thus, the Mössbauer spectroscopy with the $^{67}\text{Ga}(^{67}\text{Zn})$, ^{119}Sn and $^{129\text{m}}\text{Te}(^{129}\text{I})$ isotopes found no changes neither in the local symmetry of lattice sites, nor in electronic structure of atoms, nor in a strength of the electron-phonon interaction in the $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$ solid solutions near the gapless state.

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Н. С. Каблукова, В. А. Комаров, Е. В. Демидов, Е. Е. Христич

ВЛИЯНИЕ ЛИНЕЙНОГО РАСШИРЕНИЯ МАТЕРИАЛА ПОДЛОЖКИ НА ЯВЛЕНИЯ ПЕРЕНОСА В БЛОЧНЫХ И МОНОКРИСТАЛЛИЧЕСКИХ ПЛЕНКАХ СИСТЕМЫ ВИСМУТ-СУРЬМА*

Рассматривается влияние подложки на гальваномагнитные и термоэлектрические явления в тонких пленках твердого раствора висмут-сурьма. Выделяется два основных механизма этого влияния: через совершенство структуры пленки (влияние на структуру пленки) и через деформацию, обусловленную несоответствием линейного расширения материала подложки и пленки. Приводится сравнение свойств блочных текстурированных пленок с монокристаллическими, полученными методом зонной перекристаллизации под покрытием.

Ключевые слова: висмут-сурьма, тонкие пленки, монокристаллические пленки, явления переноса, гальваномагнитные явления, размерный эффект, механическая деформация пленок.

*N. Kablukova, V. Komarov,
E. Demidov, E. Khristich*

The Influence of Thermal Expansion of the Substrate Material on the Transport Phenomena in Block and Single-crystal Films of Bismuth-Antimony.

The influence of the substrate on galvanomagnetic and thermoelectric properties of Bi-Sb thin films is studied. Two main mechanisms of the influence are revealed: via structure quality of films and via deformation due to the difference in thermal expansion coefficients of substrate and film materials. The comparison of properties of block textured and monocrystalline films made by the method of floating-zone refining under cover is carried out.

Keywords: bismuth-antimony, thin films, monocrystalline films, transport phenomena, galvanomagnetic phenomenon, size effect, mechanical deformation of films.

Тонкие металлические и полупроводниковые пленки представляют собой объекты с разнообразными физическими свойствами, при этом физические характеристики вещества в виде пленок могут существенно отличаться от свойств этих веществ в массивном кристалле. Это создает дополнительные проблемы в использовании пленок в качестве технических материалов и элементов аппаратуры, но одновременно изменчивость свойств тонких пленок расширяет возможности их практического применения. Знание основных закономерностей изменения свойств вещества при переходе к пленочному состоянию необхо-

* Исследование выполнено при поддержке Министерства образования и науки Российской Федерации, соглашение 14.В37.21.0891.