Electronic exchange between centres of iron in the vitreous arsenic selenide

K. U. Bobokhuzhaev[1], A. V. Marchenko[2], P. P. Seregin[✉2]

[1] Tashkent Regional Chirchik State Pedagogical Institute 104 Amir Temur Av., Chirchik 111700, Uzbekistan
[2] Herzen State Pedagogical University of Russia, 48 Moika River Emb., Saint Petersburg 191186, Russia

Authors
Kudrat U. Bobokhuzhaev, e-mail: qudratman@mail.ru
Alla V. Marchenko, ORCID: 0000-0002-9292-2541
Pavel P. Seregin, ORCID: 0000-0001-5004-2047

Abstract. Iron atoms in vitreous arsenic selenide films form single electron donor centres, while the Fermi level shifts from the middle of the band gap to the bottom of the conduction band with an increase in the iron concentration due to the filling of single electron states of the acceptor type located below the Fermi level. The Mössbauer spectroscopy method was used to study the electronic exchange between ionised and neutral centres of iron in the glassy selenide of arsenic.

Keywords: chalcogenide glass, dopant iron atoms, electron exchange, Mössbauer spectroscopy.

Introduction

The fundamental property of the electrical inactivity of impurity atoms in chalcogenide glassy semiconductors is well-known (Marchenko, Nasredinov, Seregin 2018), although exceptions are known for some impurities. In particular, the electrical activity of iron impurity atoms was discovered in glassy films of arsenic selenide back in 1990 (Turaev, Seregin, Nasredinov 1990). Later, we undertook studies of both the nature of the electrical activity of iron (Marchenko, Luzhkov, Rasnyuk et al. 2017; Marchenko, Terukov, Egorova et al. 2017) and the mechanism of electrical activity of the different states of iron in As_2Se_3 (Bobokhuzhaev, Rabchanova, Seregin, Shaldenkova 2015; Marchenko, Rabchanova, Seregin et al. 2016). In this paper, we consider all the results we obtained (Bobokhuzhaev, Rabchanova, Seregin, Shaldenkova 2015; Marchenko, Rabchanova, Seregin et al. 2016; Marchenko, Luzhkov, Rasnyuk et al. 2017, Marchenko, Terukov, Egorova et al. 2017; Marchenko, Nasredinov, Seregin 2018; Turaev, Seregin, Nasredinov 1990) from a single perspective.

Experiment design

The modification was carried out by a high-frequency ion plasma sputtering of arsenic selenides and metal iron (enriched by ^{57}Fe isotope to 92% with the summary content of impurities < 10^{-4} at.%) in an argon atmosphere at a pressure of 10^{-2} Torr at a frequency of 13.6 MHz with the subsequent annealing of the films at 150°C for 30 min, in order to stabilise their properties. The iron concentration, N_{Fe}, varied from 0.5 to 4.0 at.% and was controlled by the method of X-ray fluorescent analysis with an error of ±0.1 at.%. The amorphism of the films was checked by the X-ray phase analysis. The ^{57}Fe Mössbauer spectra in the range of temperatures from 80 to 400 K were recorded using a ^{57}Co radiation

source in a palladium matrix. The electro conductance temperature dependence and the Seebeck coefficient sign were measured using standard methods. The error in determining the electro conductance activation energy E_σ amounted to ±0.05 eV (Marchenko, Terukov, Egorova et al. 2017). The position of the optical absorption edge for pure and doped As_2Se_3 glass was determined in the range of 600–2500 µm at 20°C; the error in determining the optical absorption edge was ±0.02 eV. Since for chalcogenide glass an exponential dependence of the absorption coefficient α on the light frequency ω is typical in the region of the absorption (Urbach) edge, a linear dependence $(\alpha\hbar\omega)^{1/2} = f(\hbar\omega)$ was built and its extrapolation on $(\alpha\hbar\omega)^{1/2} = 0$ was made (here α is the absorption coefficient, and ħ is the Planck constant), in order to measure the value of the optical band gap width E_{opt}.

Results and discussion

Electrical activity of iron atoms

According to the Seebeck coefficient, the As_2Se_3 films, which do not contain iron, possess a hole type of conductivity, while their modification results in an electron type of conductivity (at $N_{Fe} > 0.5$ at.%) (Marchenko, Terukov, Egorova et al. 2017). The introduction of iron leads to a substantial increase in the conductance σ (Fig. 1); the conductance activation energy E_σ decreases tending to a limiting value of 0.24 eV at $N_{Fe} = 4$ at.% (Fig. 2). The optical band gap for the films E_{opt} decreases with the growth of the iron concentration (Fig. 3), but not as sharply as E_σ (Fig. 2) (Marchenko, Rabchanova, Seregin et al. 2016).

The ^{57}Fe Mössbauer spectra in the modified As_2Se_3 films are shown in Figs. 4, 5. When $N_{Fe} \leq 2$ at.%, the spectra at 295 K represent quadrupole doublets (the isomeric shift $IS = 0.22 \pm 0.02$ mm/s, quadrupole splitting $\Delta = 0.64 \pm 0.03$ mm/s, and the spectral line width at half height $G = 0.31 \pm 0.03$ mm/s; these values weakly depend on the iron concentration), which correspond to iron atoms Fe^{3+} in a distorted tetrahedral environment of selenium atoms (Fig. 4) (Bobokhuzhaev, Rabchanova, Seregin, Shaldenkova 2015). When $N_{Fe} > 2$ at.%, the Mössbauer spectra are a superposition of a quadrupole doublet referring to the already described state Fe^{3+} and a quadrupole doublet ($IS = 0.82 \pm 0.02$ mm/s, $\Delta = 1.82 \pm 0.03$ mm/s, and $G = 0.31 \pm 0.03$ mm/s; these values weakly depend on the iron concentration) corresponding to the iron atoms Fe^{2+} in a distorted tetrahedral environment of selenium atoms (Fig. 4). The fraction of iron atoms Fe^{2+} increases with the growth of the total iron concentration in the films (Fig. 6) (Marchenko, Rabchanova, Seregin et al. 2016).

Thus, an introduction of iron into vitreous arsenic selenide leads to a shift of the Fermi level from the band gap middle (for undoped glass) to the conduction band bottom (for doped glass). For undoped glass $E_{opt} \approx 2E_\sigma$ and the current transfer, according to the sign of Seebeck coefficient, is realised by holes. The introduction of iron into glass leads to a change in the sign of the current carriers (the current transfer, according to the sign of the Seebeck coefficient, is realised by electrons) and to a decrease in the electro conductance activation energy (Marchenko, Rabchanova, Seregin et al. 2016).

Figure 7 presents the dependence of the shift of the Fermi level from the middle of the band gap $\delta E = (E_{opt})/2 - E_\sigma$ on the iron concentration. As can be seen from the figure, when the iron concentration increases, the Fermi level smoothly approaches its limiting position, which is distant from the middle of the band gap by a value of 0.57 ± 0.03 eV (Marchenko, Rabchanova, Seregin et al. 2016).
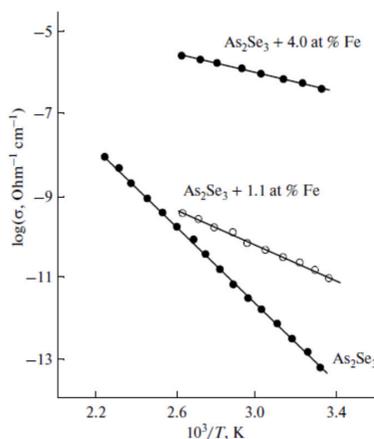

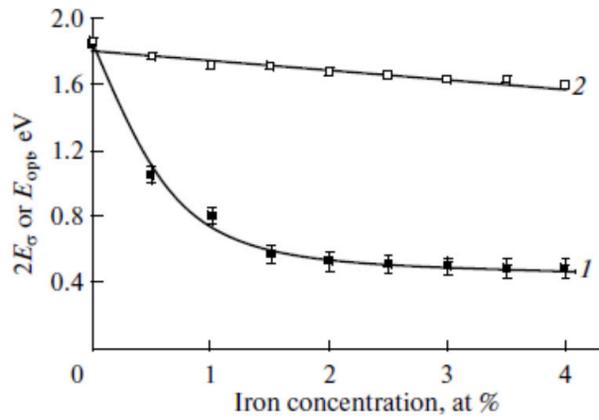Fig. 1. Electroconductance temperature dependences for As_2Se_3 films and As_2Se_3 films modified with iron

Fig. 2. Dependence of the electroconductance activation energy E_σ (1) and the optical band gap E_{opt} (2) of modified As_2Se_3 films on the iron concentration
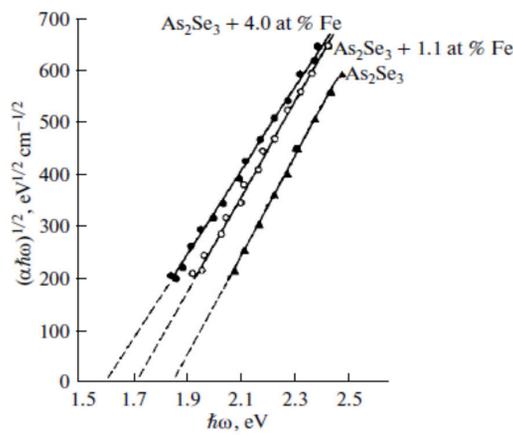
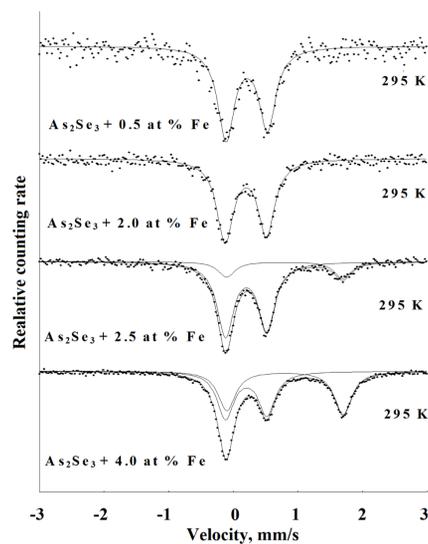

Fig. 3. Optical absorption edge of iron films

Fig. 4. Mössbauer spectra for ^{57}Fe atoms in modified As_2Se_3 films at room temperature in the range of concentrations of 0.5–4.0 at. % Fe. The decomposition of the experimental spectra into two quadrupole doublets is shown, which correspond to the Fe^{3+} and Fe^{2+} states

Fig. 5. Mössbauer spectra for ^{57}Fe atoms in modified As$_2$Se$_3$ films at 80 and 440 K at concentration of 2 and 3 at. % Fe. The decomposition of the experimental spectra into two quadrupole doublets is shown, which correspond to the Fe^{3+} and Fe^{2+} states
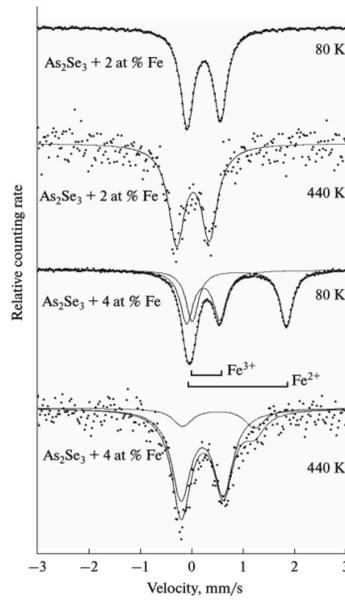
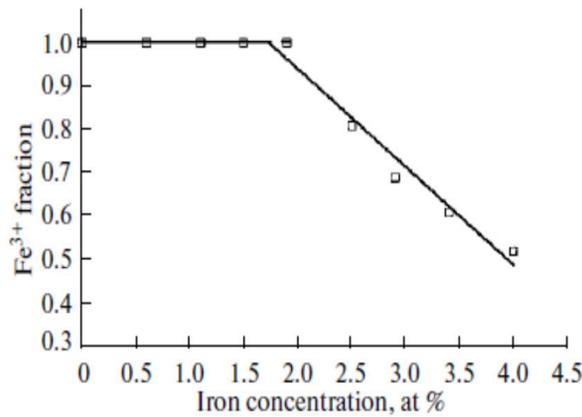

Fig. 6. Dependence of the Fe^{3+} fraction on the total iron concentration in the ^{57}Fe Mössbauer spectra of As$_2$Se$_3$
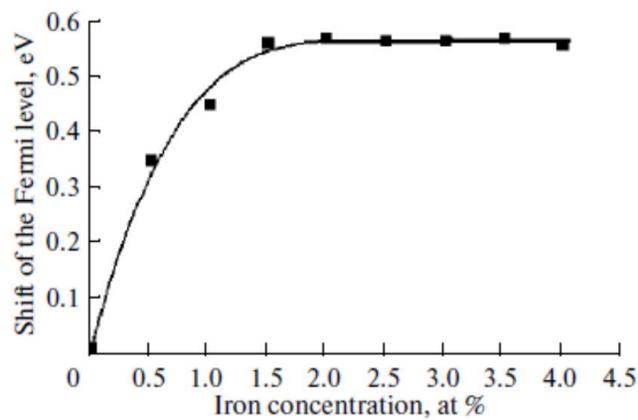

Fig. 7. Dependence of the shift of the Fermi level from the middle of the band gap
$\delta E = (E_{opt})/2 - E_\sigma$ on the iron concentration

In order to explain the experimental data, we should assume that the iron atoms form a single-electron level of a donor type in the band gap. In other words, when an iron atom penetrates into a glass structural network, it forms chemical bonds with the chalcogen atoms using two valence 4s electrons coupled by the spin (i.e., the state Fe^{2+} of iron oxidation is formed), while one uncoupled valence $3d$ electron of an iron atom plays the role of a donor electron with an ionization energy of 0.24 ± 0.03 eV (the energy is counted from the bottom of the conduction band) (Fig. 2). If $N_{Fe} \leq 2$ at.%, then all the donor iron centres are ionised and only the iron Fe^{2+} state is observed in the ^{57}Fe Mössbauer spectra (Fig.4) (Marchenko, Rabchanova, Seregin et al. 2016). The fraction of the Fe^{2+} ions can be calculated using the following equation:

$$p = \frac{s_n^{80}}{s_n^{80} + s_i^{80}}, \qquad (1)$$

where s_n^{80} and s_i^{80} are the areas under the Mössbauer spectra recorded at 80 K and corresponding to the Fe^{2+} and Fe^{3+} ions, respectively. In other words, under the conditions of film preparation, the concentration of acceptor type intrinsic defects in glass, which compensate the donor iron centres by transferring them from the Fe^{2+} state into the Fe^{3+} state, amounts to less than 2 at.%. However, these electrons do not enter into the conduction band; instead, they fill local states having a continuous energy distribution from the top of the valence band to the bottom of the conduction band. This results in the shift of the Fermi level from the middle of the band gap to the bottom of the conduction band; the higher the iron concentration, the larger this shift (Bobokhuzhaev, Rabchanova, Seregin, Shaldenkova 2015).

Naturally, when the Fermi level reaches an iron donor level (this happens at $N_{Fe} \sim 2$ at.%), then a part of the iron centres turns out to be in a nonionised state, and the component corresponding to Fe^{2+} appears in the ^{57}Fe Mössbauer spectrum. The iron Fe^{2+} fraction at $N_{Fe} > 2$ at.% will increase with the iron concentration growth, which is observed in the Mössbauer spectra (Figs. 4, 5) (Bobokhuzhaev, Rabchanova, Seregin, Shaldenkova 2015).

The maximum shift in the Fermi level (~ 0.57 eV) corresponds to the energy position of the level of the iron donor to the middle of the band gap. The monotonic decrease in the conductance activation energy of the iron As_2Se_3 films by the increase of the iron concentration is explained by the shift of the Fermi level described above.

A small decrease in the optical width of the band gap for As_2Se_3 arsenic selenide modified with iron is explained by the formation of a solid solution in glass based on arsenic selenides and iron selenides with one of the solid solution components (iron selenide) being a narrow band gap semiconductor (Bobokhuzhaev, Rabchanova, Seregin, Shaldenkova 2015).

Electronic exchange between centres of iron

It is obvious that when the Fermi level is close to the level of iron, the electron exchange between the two oxidation states of iron (Fe^{2+} and Fe^{3+}) is possible, which should give rise to the convergence of the central shift values of the Mössbauer spectra of the Fe^{2+} and Fe3+ sites. In the limit of fast electron exchange, when the lifetimes of the Fe^{2+} and Fe^{3+} states are much shorter than the lifetime of the ^{57}mFe nuclear isomer ($\sim 10^{-7}$ s), the Mössbauer spectrum of the averaged state of iron with the following central shift should be (Marchenko, Luzhkov, Rasnyuk et al. 2017):

$$S = \frac{S_i^{80} + P S_n^{80}}{P + 1}, \qquad (2)$$

where

$$P = \frac{N_{Fe^{2+}}}{N_{Fe^{3+}}} \leq 1, \qquad (3)$$

S_n^{80} and S_i^{80} are the central shifts of the Mössbauer spectra recorded at 80 K and corresponding to the Fe^{2+} and Fe^{3+} sites, respectively.

The temperature dependences of the central shifts of the Mössbauer spectra of Fe^{3+} and Fe^{2+} sites at NFe = 2 at.% (when P ≈ 0) and NFe = 4 at.% (when P ≈ 1) are shown in Fig. 8 (Marchenko, Luzhkov, Rasnyuk et al. 2017)

For the case when P ≈ 0, only the quadrupole doublet corresponding to the Fe^{3+} ion is present in the Mössbauer spectrum, the central shift of which in the range of temperatures from 80 to 440 K only slightly decreases with an increase in the temperature, which can be explained by the manifestation of the transverse Doppler effect. In most cases, the central shift S of the Mössbauer spectra is determined by the isomeric shift δ and the squared Doppler shift D.

$$S = \delta + D, \tag{4}$$

and the temperature dependence of the central shift is determined by the temperature dependence of the D value, which looks as follows in the Debye approximation:

$$D = -\frac{3}{2}E_0\frac{k\Delta T}{Mc^2}f\left(\frac{\Delta T}{\theta}\right), \tag{5}$$

where E_0 is the energy of the isomeric transition for the ^{57m}Fe isotope, k is the Boltzmann constant, M is the mass of the irradiating ^{57}Fe atom, c is the speed of light in vacuum, θ is the Debye temperature of the investigated material, $f\left(\frac{\Delta T}{\theta}\right)$ is the Debye function, and ΔT is the difference between the temperatures at which the Mössbauer spectra of the sample are recorded (Marchenko, Luzhkov, Rasnyuk et al. 2017).

The theoretical temperature dependences of the squared Doppler shift of the Mössbauer spectrum of the ^{57}Fe isotope (the used Debye temperatures are 120 and 200 K) and the experimental temperature dependence of the central shift of the Mössbauer spectrum of the Fe^{3+} sites at P ≈ 0 are shown in Fig. 9. As seen from the plots, there is satisfactory agreement between the theoretical and experimental dependences.

For the case when P ≈ 1, two quadrupole doublets corresponding to the Fe^{3+} and Fe^{2+} sites are present in the Mössbauer spectrum, the central shifts of which become close to each other with an increase in the temperature (see Fig. 8), the spectral lines are broadened (Fig. 10), and the relative area under the spectrum corresponding to Fe^{2+} sites is decreased (Fig. 11) (Marchenko, Luzhkov, Rasnyuk et al. 2017).
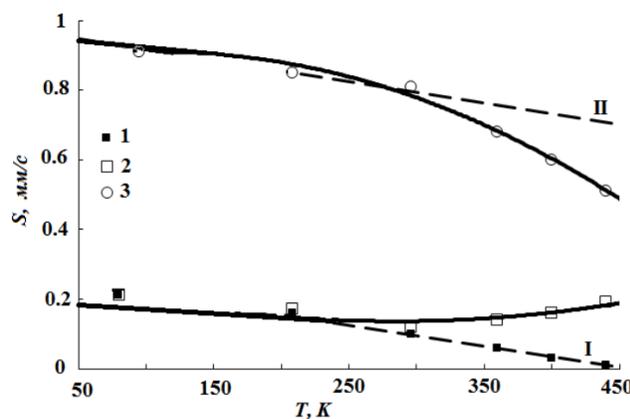

Fig. 8. Temperature dependences of the central shifts of the Mössbauer spectra of Fe^{3+} sites in As_2Se_3 films for an iron concentration of *(1)* 2 and *(2)* 4 at.%, and *(3)* of Fe^{2+} sites for an iron concentration of 4 at.%; the dashed lines correspond to the temperature dependences of the central shifts of the Mössbauer spectra of the (I) Fe^{3+} and (II) Fe^{2+} sites, which are determined from the temperature dependences of the squared Doppler shifts in the ^{57}Fe Mössbauer spectra
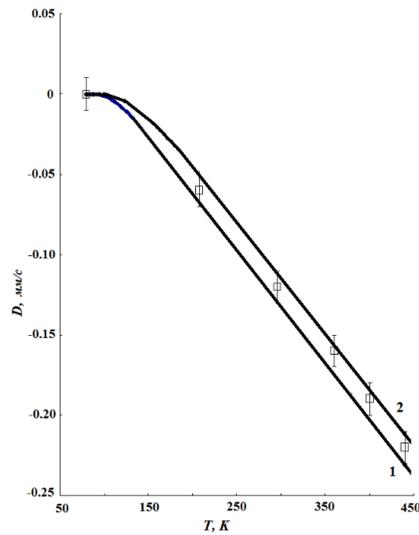
Fig. 9. Theoretical temperature dependences (solid lines) of the Doppler shift of the Mössbauer spectrum on the ^{57}Fe isotope for Debye temperatures of *(1)* 120 and *(2)* 200 K and the experimental temperature dependence of the central shift of the Mössbauer spectrum of the Fe^{3+} sites in As_2Se_3 films for an iron concentration of 2 at.%
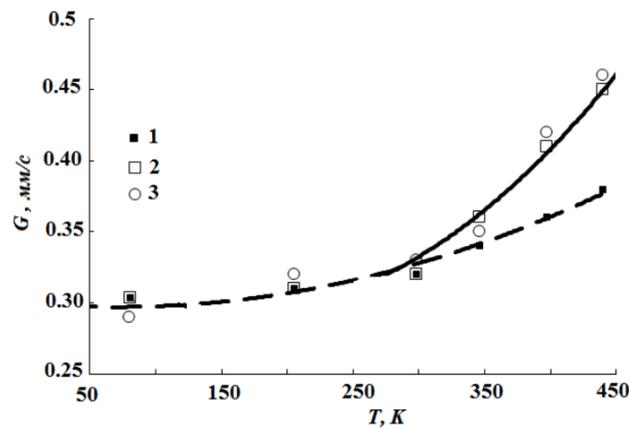

Fig. 10. Temperature dependences of the spectral line widths of the Mössbauer spectra of Fe^{3+} sites in As_2Se_3 films for an iron concentration of *(1)* 2 and *(2)* 4 at.%, and *(3)* of Fe^{2+} sites for an iron concentration of 4 at.%

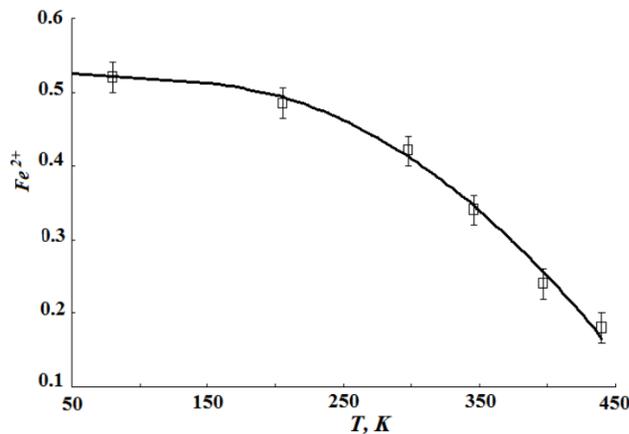Fig. 11. Temperature dependence of the fraction of Fe^{2+} sites in the Mössbauer spectra of As_2Se_3: 57Fe at N_{Fe} = 4 at.%

The spectra in Fig. 5 and results of their processing in Fig. 8 and Fig. 10 illustrate the typical pattern of the electron exchange between the two iron oxidation states, Fe^{2+} and Fe^{3+}. A decrease in the relative area under the spectrum corresponding to Fe^{2+} sites does not indicate a decrease in the concentration of Fe^{2+} sites with an increase in the temperature, but a more distinct dependence of the Mössbauer coefficient on the temperature for the compounds of doubly charged iron in comparison with the compounds of Fe^{3+} (Marchenko, Luzhkov, Rasnyuk et al. 2017).

Considering that the local symmetry of Fe^{2+} and Fe^{3+} sites is lower than cubic symmetry, it is reasonable to expect the electron exchange to be accompanied by a change in the tensor of the electric field gradient (EFG); i.e., the quadrupole splittings of the Fe^{2+} and Fe^{3+} Mössbauer spectra should change with an increase in the temperature.

In fact, if the local symmetry of the ^{57m}Fe Mössbauer probe is lower than its cubic symmetry, then the energy level of the ^{57m}Fe nucleus decomposes into two sublevels as a result of the interaction of the quadrupole moment Q of the iron nucleus with the EFG tensor on it, and the quadrupole splitting of the Mössbauer spectrum arises (Marchenko, Luzhkov, Rasnyuk et al. 2017). The Laplace equation $U_{xx} + U_{yy} + U_{zz} = 0$ is applicable for a diagonalised EFG tensor, and this EFG tensor is determined by the following two parameters: the main component U_{zz} of the EFG tensor and the asymmetry parameter $\eta = \dfrac{U_{xx} - U_{yy}}{U_{zz}}$ (here x, y, and z are the main axes of the EFG tensor, which are chosen based on the inequality $|U_{xx}| \le |U_{yy}| \le |U_{zz}|$). The Mössbauer spectrum is represented by a doublet with the following distances between the components:

$$\Delta = \frac{1}{2}eQU_{zz}\left(1 + \frac{\eta^2}{3}\right)^{1/2}. \qquad (6)$$

In general, there are the following two EFG sources on the atomic nuclei: the ions of the structural lattice of glass (they produce crystalline EFG) and no spherical valence electrons of the Mössbauer atom (they produce valence EFG). Accordingly,

$$U_{zz} = (1 - \gamma)V_{zz} + (1 - R_o)W_{zz}, \qquad \eta = \frac{(1 - \gamma)V_{zz}\eta_{cr} + (1 - R_o)W_{zz}\eta_{val}}{U_{zz}}, \qquad (7)$$

where U_{zz}, V_{zz}, and W_{zz} are the main components of the total, crystalline, and valence EFG tensors, respectively; η, and η_{cr}, η_{val} are the asymmetry parameters of these tensors; γ and R_0 are the Sternheimer coefficients (they take into account the shielding and deshielding of EFG produced by the external charges and by the internal electron shells of the probe atom).

If the valence shells of the Mössbauer atom are completely or half-filled (the Fe^{3+} ion is a typical example), then only the charges of neighbour atoms should be taken into account for such an atom upon the calculations of EFG; the Δ value in this case is insignificant, and its temperature dependence is determined by the temperature dependences of the interatomic distances in the crystal and in the structural lattice of glass, and this dependence is, as a rule, very weak. However, if the valence shells of the Mössbauer atom are filled only partially (Fe^{2+} is a typical example), then the valence electrons are the main source of EFG; therefore, the Δ value is significantly increased, and it noticeably decreases upon an increase in the temperature (Marchenko, Luzhkov, Rasnyuk et al. 2017).

The temperature dependences of the quadrupole splittings of the ^{57}Fe Mössbauer spectra corresponding to the Fe^{2+} and Fe^{3+} sites are shown in Fig. 12. It is seen that a small value of the quadrupole splitting Δ_i and its insignificant decrease with an increase in the temperature are observed in the range of temperatures from 80 to 400 K for the case with an iron concentration of less than 2 at.% (iron is stabilised only in the Fe^{3+} state), as expected for the triply-charged Fe^{3+} state of iron. In the case with an iron concentration of 4 at.% (iron is stabilised in the two equally populated Fe^{2+} and Fe^{3+} states), small values of the quadrupole splitting Δ_i and their decrease with an increase in the temperature are observed in the Mössbauer spectra of the Fe^{3+} sites in the range of temperatures from 80 to 350 K, whereas the Δ_i value starts to increase anomalously upon a further increase in the temperature. For the spectra of Fe^{2+} sites, the quadrupole splitting value Δ_{ii} for the same samples is significantly larger, and the rate of its decrease upon an increase in the temperature has the following two areas: the area at the temperatures ranging from 80 to 350 K,

in which the quadrupole splitting considerably decreases, and the area at T > 350 K, in which this decrease becomes more rapid.

Thus, the quadrupole splitting values of the Mössbauer spectra of the Fe^{3+} and Fe^{2+} sites in the films of arsenic selenide glass approach each other upon an increase in the temperature, which indicates that the EFG tensor parameters produced on the atomic nuclei of the neutral and ionised iron donor centres become closer.
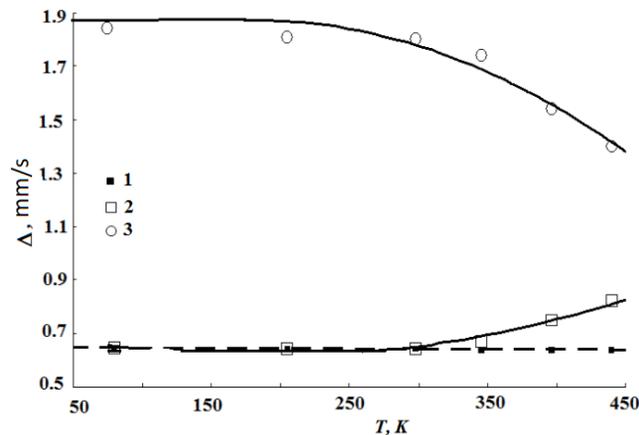

Fig. 12. Temperature dependences of the quadrupole splitting of the Mössbauer spectra of Fe^{3+} sites in As_2Se_3 films for an iron concentration of *(1)* 2 and *(2)* 4 at. %, and *(3)* of Fe^{2+} sites for an iron concentration of 4 at.% *(3)*

Conclusion

In glass films of arsenic selenide modified by iron, the Fe^{2+} and Fe^{3+} sites corresponding to the neutral and ionised states of the one-electron donor iron centre are detected. Both the central shift and quadrupole splitting values of the Mössbauer spectra of the Fe^{3+} and Fe^{2+} sites become closer upon an increase in the temperature, which indicates that the electronic densities and EFG tensor parameters on the atomic nuclei of the neutral and ionised iron donor centres are equalised.

References

Bobokhuzhaev, K. U., Rabchanova, T. Yu., Seregin, P. P., Shaldenkova, A. V. (2015) Elektricheskaya aktivnost' primesnykh atomov zheleza v stekloobraznykh selenidakh mysh'yaka [Electrical activity of iron impurity atoms in vitreous arsenic selenide]. *Izvestiya Rossijskogo gosudarstvennogo pedagogicheskogo universiteta im. A. I. Gertsena — Izvestia: Herzen University Journal of Humanities & Sciences*, 176, 61–71. (In Russian)

Marchenko, A. V, Luzhkov, A. A., Rasnyuk, A. N. et al. (2017) Electron exchange between dopant iron sites in glass films of arsenic selenide. *Glass Physics and Chemistry*, 43, 158–162. DOI: 10.1134/S1087659617020092 (In English)

Marchenko, A. V., Rabchanova, T. Yu., Seregin, P. P. et al. (2016) Origin of the electrical activity of iron atoms in vitreous arsenic selenide. *Glass Physics and Chemistry*, 42, 246–250. DOI: 10.1134/S1087659616030081 (In English)

Marchenko, A. V., Terukov, E. I., Egorova, A. Yu. et al. (2017) Electron exchange between neutral and ionized impurity iron centers in vitreous arsenic selenide. *Semiconductors*, 51, 449–453. DOI: 10.1134/S1063782617040133 (In English)

Marchenko, A., Nasredinov, F., Seregin, P. (2018) *Dynamics of the two-electron processes in impurity semiconductors. Mössbauer spectroscopy of impurity centers of tin and germanium in crystalline and glassy chalcogenide semiconductors.* Beau Bassin: LAP Lambert Academic Publishing, 390 p. (In English)

Turaev, E. Yu., Seregin, P. P., Nasredinov, F. S. (1990) Tin and iron impurity atom states in modified As_2Se_3 films. *Physica Status Solidi (B)*, 161 (1), 287–292. DOI: 10.1002/pssb.2221610128 (In English)