

Study of platinum impurity atom state in vitreous arsenic selenide

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Platinum atoms in the structure of As_2Se_3 glass are stabilized in the form of Pt^{2+} and Pt^{4+} ions and correspond to ionized states of the amphoteric two-electron center with negative correlation energy (Pt^{2+} is an ionized acceptor, and Pt^{4+} is an ionized donor), whereas the neutral state of the Pt^{3+} center appears to be unstable.

1. Introduction

To describe the behavior of impurity atoms in chalcogenide glassy semiconductors, the concepts of the existence of two-electron with negative correlation energy (negative U-centers) in the glass structural network are widely used [1]. These concepts were developed by Street and Mott [2] and Kastner, Adler, and Fritzsche [3]. Drabkin and Moizhes [4] first considered the possibility of stabilizing negative U-centers in IV–VI semiconductors. They identified negative U-centers with resonant states of indium and thallium impurities in lead chalcogenides. Bishop, Strom, and Taylor [5–7] examined optically induced localized paramagnetic states in chalcogenide glassy semiconductors by electron spin resonance and explained why negative U-centers could not be observed while using electron spin resonance standard registration methods. Negative U-centers of tin were detected for the first time by the method of ^{119}Sn Mössbauer spectroscopy in chalcogenide glasses [8–10]. The existence of two valence states Sn^{2+} and Sn^{4+} for tin, differing by $2e$, may be the reason for formation negative U-centers in the glass by tin. From this point of view platinum impurity atoms are of great interest, because the valence states Pt^{2+} and Pt^{4+} are also possible for platinum.

This work is devoted to the study of the states of platinum impurity atoms of vitreous As_2O_3 . Mössbauer spectroscopy and electron spectroscopy were used, also the temperature dependence of conductivity of pure and doped glasses was measured.

2. Experimental techniques

Vitreous As_2Se_3 was synthesized by melting together arsenic and selenium (99.999% pure) at $950^\circ C$ in quartz ampoules evacuated to 10^{-4} Torr. The glasses were doped with platinum by alloying As_2Se_3 with platinum metal, with the concentration of platinum 0.1 at.%. Metallic Pt, enriched by ^{196}Pt up to 96%, had been previously irradiated with a thermal neutron flux of $\sim 10^{19}$ neutrons/cm². Glasses were

synthesized by melting arsenic selenide As_2Se_3 and platinum in evacuated (to a residual pressure of 10^{-3} mm Hg) thin-walled silica glass tubes at a temperature of 1250 K for 4 h with vibrational stirring of the melt. Then, the melt sample weighing 5 g was quenched either in air, or by pouring the melt onto a metal slab cooled with liquid nitrogen from the temperature of the melt (1050 or 1250 K). The criteria of the vitreous state were as follows: X-ray diffraction patterns, a characteristic conchoidal fracture and the absence of microincorporations, as defined by surface scanning under a MIM-8 microscope.

The electrical conductivity of alloys was measured using the ground samples in the form of disks over the temperature range 295 to 390 K. The error of activation energy for conductivity was ± 0.02 eV.

Platinum electron spectra ($4f_{7/2}$ lines) were recorded using a Hewlett Packard spectrometer. The binding energy of carbon $1s_{1/2}$ electrons was accepted to be 284.5 eV. The error of electron binding energy evaluation was ± 0.1 eV.

^{197}Au Mössbauer spectra were recorded using an electrodynamic spectrometer at 4.2 K. Metallic gold was used as a standard absorber for emission spectra measurements. The surface density of absorbers was 250 mg/cm² as reduced to gold. The isomer shifts are given relative to a metallic Pt source. The error of isomer shift δ measurement was ± 0.10 mm/s, that of line width G and quadrupole splitting Δ measurements was ± 0.15 mm/s.

3. Experimental results and discussion

The X-ray amorphous As_2Se_3 samples, doped with platinum, have been obtained only at platinum concentrations lower than 1 at.%. Higher concentrations resulted in glass-crystal samples, in which the X-ray analysis showed the $PtAs_2$ phase.

As it is seen from Fig. 1 both for pure and doped As_2Se_3 the temperature dependence of conductivity is given by the formula $\sigma = \sigma_0 \exp(-E_0/kT)$. The activation energy for electroconductivity E_0 does not depend on the existence of platinum and equals 1.6 eV.

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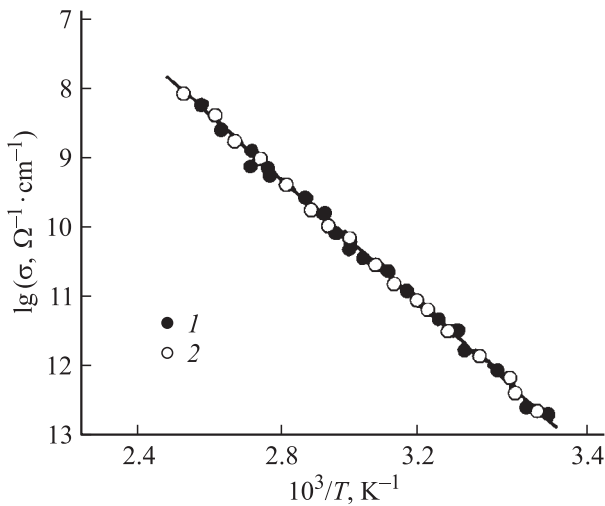


Figure 1. Temperature dependences of conductivity for As_2Se_3 glasses pure (1) and doped with platinum (2); the metal concentrations were 0.2 at.%.

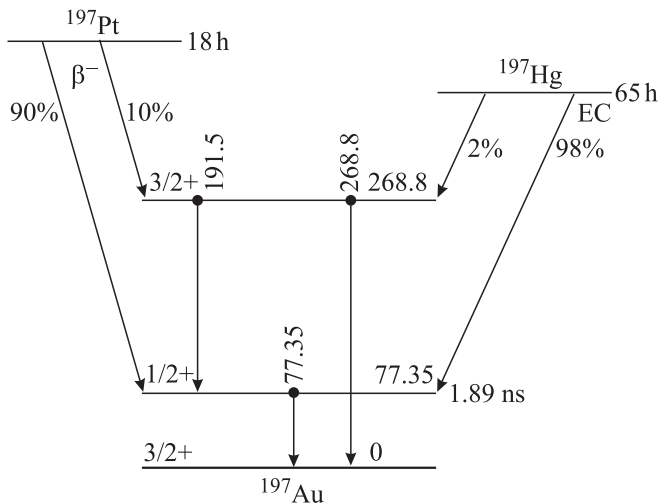


Figure 2. Decay scheme of ^{197}Pt .

The $^{197}Pt(^{197}Au)$ Mössbauer emission spectra were interpreted by assuming that the ^{197}Pt parent isotope in the structure of glassy form intrinsic structural units. In the samples under investigation, there occur the decay of the ^{197}Pt and the formation of the ^{197}Au level with an energy of 77.4 keV and a lifetime of $\sim 1.89 \cdot 10^{-9}$ s (see Fig. 2). The electron shell of the gold atom formed in this case has managed to transform in a time of $\sim 10^{-12}$ s; however, its nearest environment relaxes for a time of $\sim 10^{-8}$ s and has not managed to change during the lifetime of the ^{197}Au Mössbauer level. Therefore, the isomer shift in the $^{197}Pt(^{197}Au)$ Mössbauer emission spectra provides information of the charge state of the gold atoms, whereas the quadrupole splitting characterizes the symmetry of the local environment of the platinum atoms.

The Mössbauer emission spectra of ^{197}Pt impurity atoms in vitreous As_2Se_3 are shown in Fig. 3. The

spectrum consists of four lines. When choosing a model for the treatment of the Mössbauer spectrum, we based on the evidence of the photoelectron spectroscopy. The $4f_{7/2}$ electron spectrum of platinum in vitreous As_2Se_3 is given in Fig. 4. The spectrum consists of two bands which correspond to two different states of platinum in As_2Se_3 sample. Basing on this evidence, we expanded the Mössbauer spectrum in Fig. 3 into two quadrupole doublets with different quadrupole splitting values: $\delta_1 =$

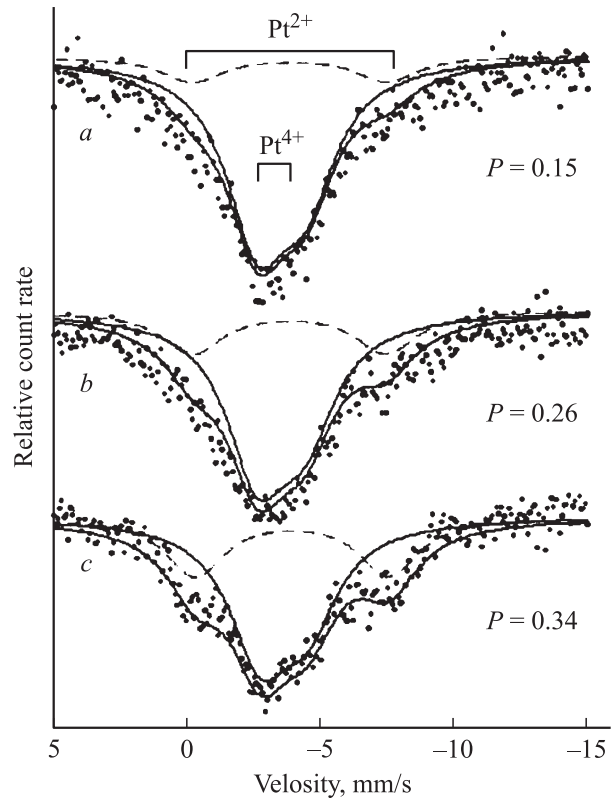


Figure 3. The $^{197}Pt(^{197}Au)$ Mössbauer spectra of the As_2Se_3 glasses at 4.2 K. The melt was quenched from 1050 K in air (a), by pouring onto a metal plate cooled with liquid nitrogen (b), and quenched from 1250 K by pouring onto a metal plate cooled with liquid nitrogen (c). The spectra corresponding to the bivalent platinum Pt^{2+} and tetravalent Pt^{4+} are shown. P — the fraction of Pt^{2+} ions in the structure of the As_2Se_3 glass.

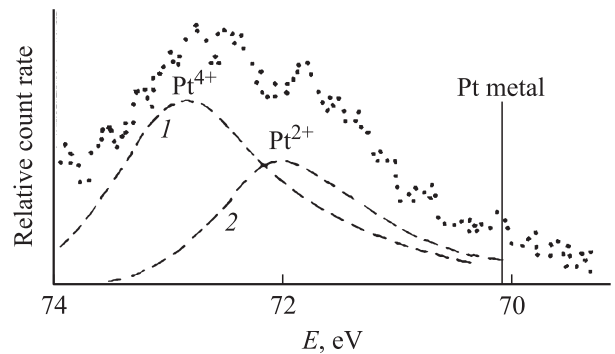


Figure 4. Electron spectrum of platinum in As_2Se_3 glass (0.2 at.% Pt).

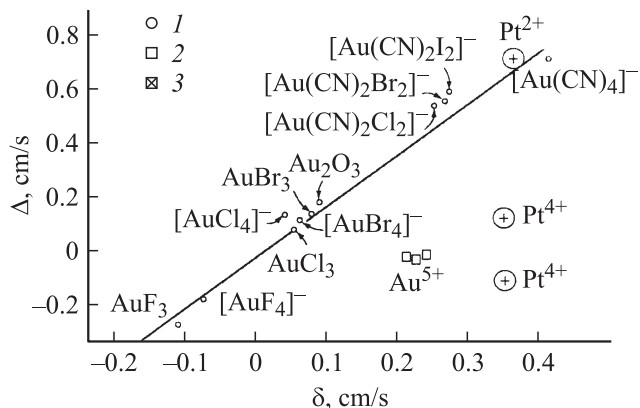


Figure 5. Quadrupole splitting-isomer shift diagram for the ¹⁹⁷Au Mössbauer spectra. 1 — data for Au³⁺ compounds [4], 2 — data of for Au⁵⁺ compounds [4], 3 — our data of for Pt in vitreous As₂Se₃.

= (3.8 ± 0.1) mm/s, Δ₁ = (7.2 ± 0.2) mm/s (spectrum a) and δ₂ = (3.5 ± 0.1) mm/s, Δ₂ = (1.8 ± 0.2) mm/s (spectrum b).

Isomer shift and quadrupole splitting values apart from each other do not allow to define the valence state of gold atoms. However, there are correlations between δ and Δ of various charge (valence) states of gold, typical for each state. These correlations were found and are given for Au-B^{III} compounds by the expression [11]

$$\Delta = 1.74 \delta - 0.22 \tag{1}$$

and for Au-B^I compounds by

$$\Delta = 1.06 \delta + 5.05 \tag{2}$$

where δ and Δ are in mm/s and isomer shifts are measured relative to metallic platinum source. The plots, representing these equations, are shown in Fig. 5.

If one used the values δ₁ = 3.8 mm/s and Δ₁ = 7.2 mm/s in the diagram in Fig. 5, the corresponding point would lie on the line, characterizing the Au-B^{III} compounds. In the electron spectrum should be related to the line with binding energy E_b = 71.8 eV, because its intensity increases as the platinum concentration increases.

Evidently, there is the direct relation between the valence state of the parent atom ¹⁹⁷Pt and the valence state of the product atom ¹⁹⁷Au, formed from ¹⁹⁷Pt after the β-decay. The states Au⁺⁵ and Au⁺³ appear after the β-decay of Pt⁺⁴ and Pt⁺² states, relatively. Thus, the spectrum 1 (Fig. 4) corresponds to the atoms of the bivalent platinum in the glass structure network. The bivalent state of platinum is also supported by the value of the 4f_{7/2} electron binding energy — the binding energy for the platinum impurity atom is higher than that for metallic platinum (see Fig. 4) which agrees with the general tendency of E_b increase as the metal valence rises.

The Mössbauer spectrum 2, Fig. 4 (with lower quadrupole splitting value) and the line with E_b = 72.5 eV

in the electron spectrum correspond to the second state of platinum impurity atoms in the structure network of vitreous As₂Se₃. The parameters of the Mössbauer spectrum 2, Fig. 4 don't meet the relationships (1) and (2), that is, the ¹⁹⁷Au atom resulting from β-decay, of ¹⁹⁷Pt, is neither Au¹⁺ nor Au³⁺. In [11] a number of compounds of gold in pentavalent state was studied, the results of the work are also shown in Fig. 5 — it is seen that the parameters of spectrum 2 are close to those of the spectra of Au⁵⁺ compounds (the point, corresponding to this spectrum is shown twice in Fig. 5 because of the sign uncertainty of Δ). This supports the suggestion that gold observed in spectrum 2 is also pentavalent, whereas the parent platinum atom in vitreous As₂Se₃ was tetravalent. The tetravalent state of platinum is also supported by the value of the 4f_{7/2} electron binding energy — the binding energy for the platinum impurity atoms is higher than that for metallic platinum and Pt²⁺ (see Fig. 4).

The Mössbauer spectra of glasses demonstrate that platinum ions in the structure of the glasses under investigation can be stabilized in two oxidation states, namely, Pt⁴⁺ and Pt²⁺, the symmetry of the local environment of the Pt⁴⁺ and Pt²⁺ atoms is different. The fraction of doubly charged Pt²⁺ ions in the structure of the As₂Se₃ glass was determined from the ratio $P = \frac{S-II}{S-II+S-IV}$, where S-II and S-IV are the areas under the spectra of Pt²⁺ and Pt⁴⁺, respectively. The error in the determination of the fraction of Pt²⁺ ions in the structure of the glass was equal to ±0.05. The fraction of doubly charged Pt²⁺ ions in the structure of the glasses increases both with an increase in the rate of quenching of the melt and with an increase in the temperature of the melt (as is clearly seen from spectra in Fig. 3). The appearance of Pt³⁺ was not observed in Mössbauer spectra of glasses. Such behavior of platinum impurity atoms can be explained by assuming that platinum in the glass structure forms negative U-centers.

Two-electron centers with negative correlation energy can exist in three charge states: D²⁺, D⁺, and D⁰ for the donor centers and A⁺, A⁰, and A⁻ for amphoteric centers; they correspond to zero, one, and two electrons at the center, respectively. It is obvious that the intermediate charge state of such centers is unstable; for it, the disproportionation reaction occurs: 2D⁺ → D⁰ + D²⁺ or 2A⁰ → A⁻ + A⁺.

Therefore, identification of negative U-centers by Mössbauer spectroscopy amounts to the following: the detection of two charged states of the center, differing by 2e (e is the elementary charge), and the detection of the dependence of populations of these states on the chemical potential position, and fixing the absence of an intermediate charge state of the center. If two charge states of the center have identical local structures (identical coordination numbers, identical symmetry of local environment, and identical atoms in the local environment), the negative U-center is either a two-electron donor or a two-electron acceptor (neutral and doubly ionized states are stable; singly ionized state of the center is unstable). If two charge states of the

center have different local structures, the negative U-center is a two-electron amphoteric center (singly ionized donor and acceptor states are stable, the neutral state of the amphoteric center is unstable).

It can be concluded that platinum atoms in glass structure form amphoteric negative U-centers, where Pt^{4+} and Pt^{2+} states correspond to the singly ionized donor and acceptor, respectively. The electrical activity of platinum centers is confirmed by the dependence of the fine structure of $^{197}Pt(^{197}Au)$ spectra on quenching conditions: the density of the donor-type point defect and Pt_3^{2+} state population increase with the melt temperature and quenching rate. If to use only the results of the Mössbauer studies then it is impossible to determine definitely whether local distortions accompanying the appearance of negative U-centers of platinum in glasses can be described by a dynamic Jahn–Teller effect, or they arise from a major shift of the platinum atoms resulting from the changes in their charge state.

4. Conclusion

Platinum impurity atoms in the structure of As_2Se_3 glass are stabilized in the form of Pt^{2+} and Pt^{4+} ions and correspond to the ionized states of the amphoteric two-electron center with negative correlation energy (Pt^{2+} is an ionized acceptor, and Pt^{4+} is an ionized donor), whereas the neutral state of the Sn^{3+} center is unstable. The fraction of Pt^{4+} states increases with increasing of liquid-melt temperature and the velocity of case-hardening.

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