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To cite this article: V Balitska *et al* 2010 *IOP Conf. Ser.: Mater. Sci. Eng.* **15** 012054

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## Radiation-induced defects in As-Sb-S glass

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**Abstract.** Defect-related instability was studied in  $\gamma$ -irradiated  $(As_2S_3)_{1-x}(Sb_2S_3)_x$  glasses ( $x=0, 0.1, 0.2$  and  $0.3$ ) using positron annihilation lifetime spectroscopy treated within high-measurement statistics. The observed decrease in average positron lifetime in the studied glasses is explained as a renovation of destroyed covalent chemical bonds after irradiation. This process is governed by monomolecular relaxation kinetics, being described in the framework of universal configuration-coordinate model.

### 1. Introduction

For a long time, chalcogenide glasses (ChG) have attracted a high interest of researchers because of their sensitivity to external influences, such as absorbed light photoexposure and high-energy ionizing irradiation [1-3]. This unique ability is connected with specific type of radiation-induced structural defects proper to ChG, so-called coordinative topological defects (CTD), appeared as pairs of positively-charged over- and negatively-charged under-coordinated atoms [1,3]. Non-exponential post-irradiation instability observed in just-irradiated ChG was ascribed to different types of CTD [3], their relaxation kinetics tending towards bimolecular one in Ge-based [4] and single-exponential monomolecular one in As-based ChG [5].

In this work, we try to resolve the origin of this principal mismatch in structural interpretation of the above instabilities using results of positron annihilation lifetime (PAL) study for As-Sb-S ChG.

### 2. Experimental

Glassy  $g-(As_2S_3)_{1-x}(Sb_2S_3)_x$  samples ( $x=0, 0.1, 0.2, 0.3$ ) were prepared by conventional melt-quenching route from high-purity (99,9999 %) initial elemental ingredients [1,3]. The obtained ingots were cut into  $\sim 1$  mm disks and then polished to a high optical quality. To remove mechanical strains appeared after quick cooling, the ChG samples were additionally annealed during 1 hour at the temperature of 10-20 K below their glass transition.

Radiation treatment of the samples was conducted by  $\gamma$ -quanta with 1.25 MeV energy and 2 MGy absorbed dose in normal conditions of stationary radiation field created in a closed cylindrical cavity

surrounded by  $^{60}\text{Co}$  sources. No special measures were taken to prevent uncontrolled annealing of the samples, but maximum temperature in the irradiating chamber did not exceed 320-330 K.

PAL measurements were performed at room temperature in different moments after irradiation using conventional fast-fast coincidence system with an ORTEC spectrometer [6,7]. The radioactive  $^{22}\text{Na}$  isotope was used as positron source, placed between two sandwiched ChG samples. The PAL spectra were recorded in high-measurement statistics utilizing more than 5 millions of elementary annihilation events, the values of average positron lifetimes  $\tau_{\text{av}}$  being taken as numerical criterion for occurred radiation-induced changes [8].

### 3. Results and discussion

The average positron lifetimes  $\tau_{\text{av}}$  of non-irradiated  $g\text{-(As}_2\text{S}_3)_{1-x}(\text{Sb}_2\text{S}_3)_x$  and the same samples measured 1 day just after irradiation and 1 month later are presented in table 1.

**Table 1.** Average positron lifetimes  $\tau_{\text{av}}$  determined in high-measurement statistics for  $g\text{-(As}_2\text{S}_3)_{1-x}(\text{Sb}_2\text{S}_3)_x$  before and after  $\gamma$ -irradiation.

ChG composition, x	Average positron lifetime $\tau_{\text{av}}$ , ns		
	before $\gamma$ -irradiation	1 day after $\gamma$ -irradiation	1 month after $\gamma$ -irradiation
0.0	0.339	0.331	0.322
0.1	0.333	0.327	0.320
0.2	0.328	0.323	0.318
0.3	0.324	0.319	0.316

As it testified from table 1, the decrease in average positron lifetime  $\tau_{\text{av}}$  was observed in all samples tested 1 day after  $\gamma$ -irradiation, this effect being inhibited with  $\text{Sb}_2\text{S}_3$  content (increase in x parameter within studied system). The same samples studied 1 month after irradiation show additional decrease in  $\tau_{\text{av}}$  with analogous compositional trend. So the most essential changes occur in  $g\text{-As}_2\text{S}_3$ : the initial average positron lifetime of 0.339 ns drops to 0.331 ns in just after-irradiation state with further tending towards saturation to 0.322 ns during 1-month natural storage.

The observed changes testify that structural shrinkage followed by further enlargement during post-irradiation storage dominates in  $\gamma$ -irradiated  $g\text{-(As}_2\text{S}_3)_{1-x}(\text{Sb}_2\text{S}_3)_x$  samples. It means that radiation effect of molar volume decrease is non-elemental one, consisting in, at least, two opposite components. Indeed, at the basis of previous physical ageing and radiation-induced hardening study in ChG [3,9], it can be supposed that weakening of covalent bonding followed by atomic shrinkage is caused by prolonged high-energy irradiation. Apart from this radiation-induced atomic densification, the simultaneous CTD formation accompanied by additional free volume appearance owing to lack of one covalent bond on under-coordinated atom occurs. In general, the former process dominates causing overall decrease in  $\tau_{\text{av}}$  values in  $\gamma$ -irradiated ChG. The further renovation in covalent bonding leads to annihilation of under-coordinated CTD correspondingly to the observed decrease in  $\tau_{\text{av}}$  in 1-month stored ChG samples (table 1).

By accepting that metastable  $(\text{As}_4^+; \text{S}_1^-)$  atomic pairs (the subscript in CTD signature denotes electric charge of atom, while the superscript denotes local atomic coordination) formed as result of heteropolar As-S bond switching into homopolar As-As one compose the main channel of externally-induced CTD in stoichiometric  $g\text{-As}_2\text{S}_3$  [3,10], the overall topological scheme of radiation-induced CTD formation can be presented as it demonstrated on figure 1.

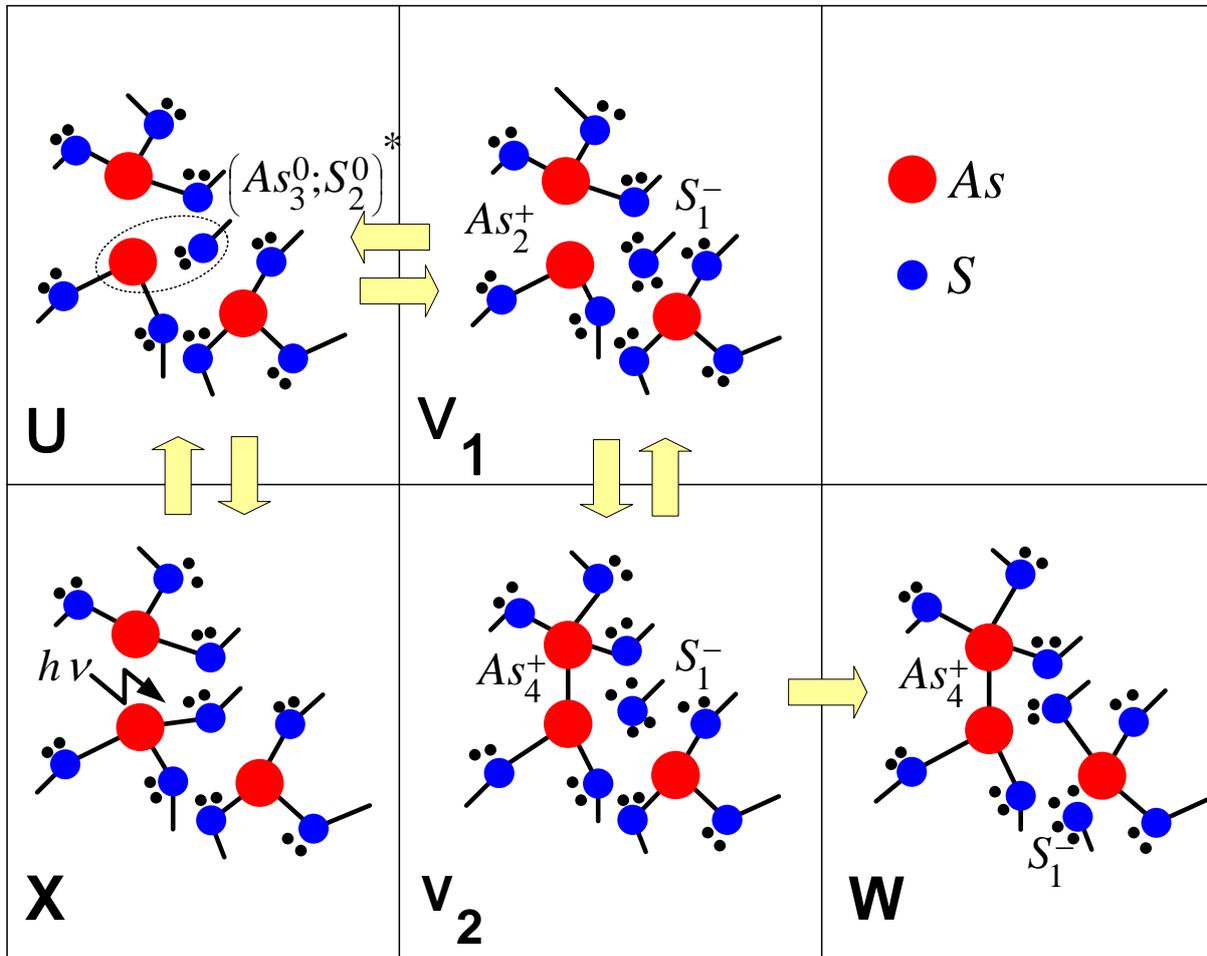


Figure 1. Defect interplay in stoichiometric g-As<sub>2</sub>S<sub>3</sub>.

The weakening in covalent linking owing to high-energy  $\gamma$ -irradiation-induced excitation of electron sub-system in g-As<sub>2</sub>S<sub>3</sub> results in destruction of basic covalent bonds of heteropolar As-S type. This process is reflected by X→U transition in figure 1. It attains a homolitical character due to difference in electronegativities of As and S atoms [1], leading to under-coordinated (As<sub>2</sub><sup>+</sup>;S<sub>1</sub><sup>-</sup>) atomic pairs being formed *in-situ* in glassy matrix. So the overall number of Lagrangian constraints per atom  $n_c$  is released in ChG during  $\gamma$ -irradiation. Thus, for atomic configurations shown in figure 1, this reduction in  $n_c$  achieves more than 10 %, providing network transformation from topologically optimally-constrained ( $n_c=3.00$ ) to under-constrained or floppy backbone ( $n_c=2.68$ ).

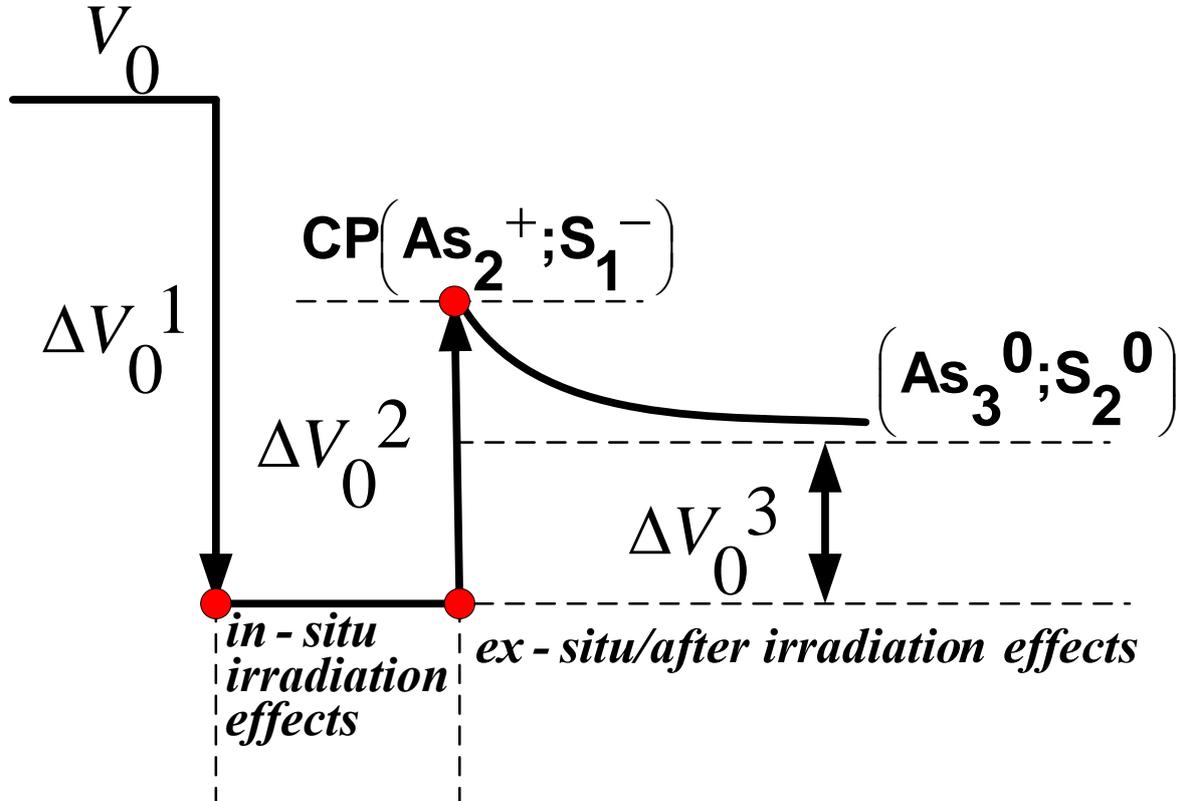
Thereby, under a prolonged irradiation (more than a few days), the ChG samples are involved in significant physical ageing, accompanied by corresponding decrease in their configurational entropy, enthalpy or free volume. This process can be characterized as *in-situ*  $\gamma$ -induced atomic densification or shrinkage. The created metastability is decomposed after irradiation tending towards initial X state owing to renovation of destroyed covalent chemical bond (V<sub>1</sub>→U→X transformation on figure 1). But latter structural transformation is only partly reversible at ambient conditions, provided temperature is far enough from glass transition region (the full restoration into initial state X is expected to be achieved beyond T<sub>g</sub>). Alternatively, the averaged covalent linking of glassy matrix can be restored through new homopolar As-As covalent bonds, which are accepted as wrong ones for chemically-ordered stoichiometric g-As<sub>2</sub>S<sub>3</sub> network. The intimate valence alternative pair or, alternatively, conjugated pair (CP) of (As<sub>4</sub><sup>+</sup>;S<sub>1</sub><sup>-</sup>) type (V<sub>2</sub> state on figure 1) is created during this process, it being correspondingly split into random pair (RP) owing to type-conserving (As-S) → (As-S) bond

switching ( $V_2 \rightarrow W$  transition on figure 1) or returned into non-defect initial state X owing to backward (As-As)  $\rightarrow$  (As-S) bond switching ( $V_2 \rightarrow X$  transition on figure 1). Whichever the case, the glassy matrix is subjected to densification due to significant radiation-induced atomic shrinkage, not fully restored at ambient temperature. These processes are mutually interconnected in dependence on intrinsic free volume distribution in ChG.

In Ge-based ChG, characterized by large input of free volume, the more decisive role belongs to CP and RP of  $(As_4^+; S_1^-)$  type. The former determine post-irradiation metastability with character time constants as high as 2-3 months [4], while the latter are responsible for thermally-reversible metastability with character thresholds near 110-120 °C [3].

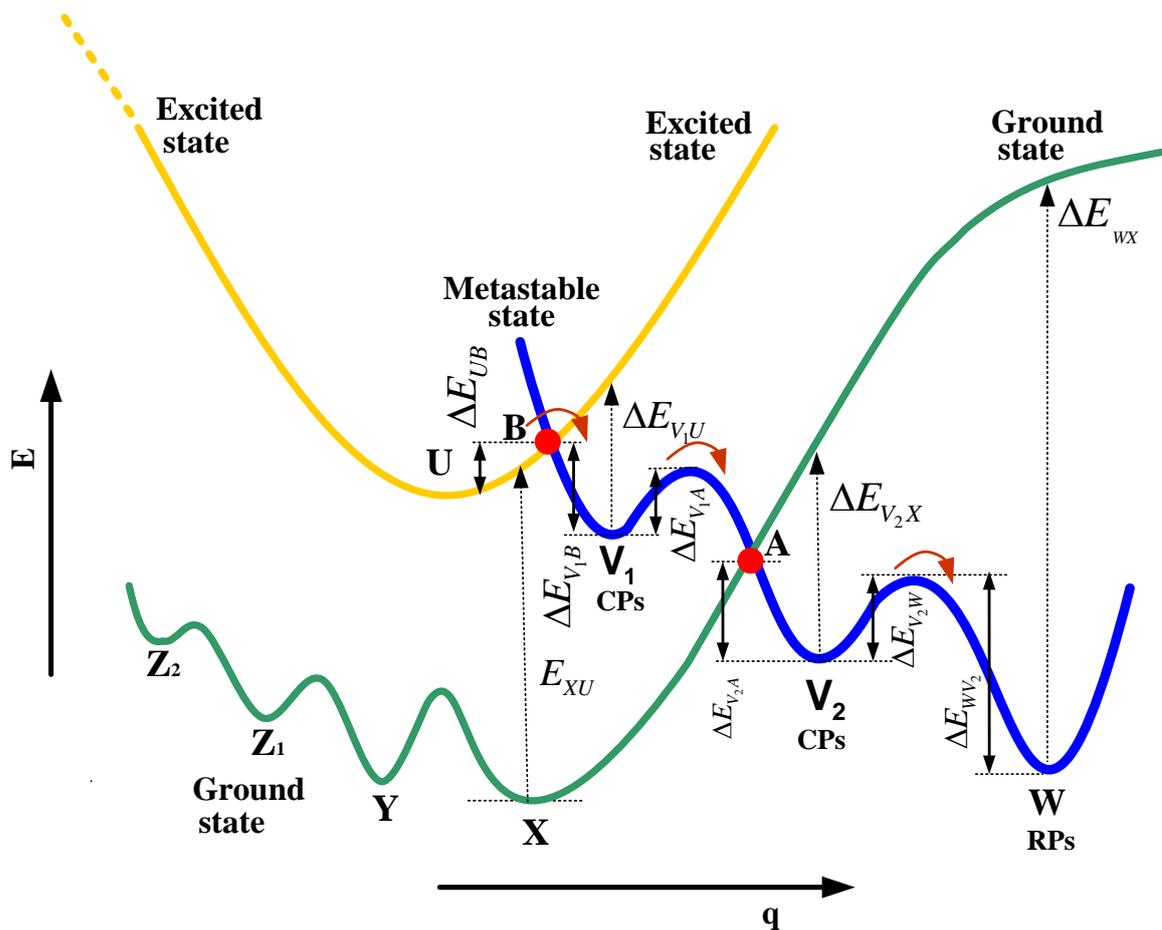
These CTD-interplay processes cardinally differ in As-based ChG. In respect to Popescu's calculations for different structural computer models of ChG [11], the more shallow nanovoids with radii below 0.3 nm can be distinguished in g-As<sub>2</sub>S(Se)<sub>3</sub>. The above  $(As_4^+; S_1^-)$  CP do not stabilize under these conditions, they being effectively transformed into RP or non-defect normally-coordinated fragments. But the part of under-coordinated  $(As_2^+; S_1^-)$  defects left after irradiation, forming the channel of quick post-radiation relaxation of single-exponential (monomolecular) type with character time constants of a few days [3].

Just this last metastability is responsible for  $\tau_{av}$  evolution in table 1. Let's imagine the initial molar volume of non-irradiated ChG to be  $V_0$ . Two independent *in-situ* processes can be attributed to this value:  $\Delta V_0^1$  – the decrease in  $V_0$  caused by “shrinkage” of under-constrained ChG network, and  $\Delta V_0^2$  – the increase in  $V_0$  owing to lack of one covalent bond localized on under-coordinated atom (figure 2). Therefore, the molar volume of ChG is effectively reduced on overall value of  $(\Delta V_0^1 - \Delta V_0^2)$ . Under normal conditions, the created  $(As_2^+; S_1^-)$  CP annihilates rapidly for a few days after irradiation turn-off with character monomolecular kinetics, like as in similar case of electron-induced dichroism [12].



**Figure 2.** Under-irradiation (*in-situ*) and post-irradiation (*ex-situ*) evolution of free volume in g-As<sub>2</sub>S<sub>3</sub> caused by under-coordinated topological defects.

These CDT-related interplay processes can be well illustrated with configuration-coordinate model in figure 3. The first element X of this model is associated with ground or initial structural state of ChG, representing itself as multi-well quasi-parabola, while the next excited state U can be presented by single parabola with wide-stretched edges in accordance to strong electron-phonon coupling proper to covalent-bonded ChG networks [1]. It should be noted this short-term state is always single-well despite a variety of external influences applied to ChG. Only vertical radiation-induced Frank-Condon-type transitions are possible between ground sub-states X, Y and Z<sub>1</sub>, ... and excited state U. The third element of the above model is associated with different CTD-related metastable states (V<sub>1</sub>, V<sub>2</sub>, W, ...), which can be presented as a parabolic-shaped curve crossing with both excited U and ground-state parabolas X in points B and A, respectively, and splitting into 3 (or even more) parabolic-like sub-states in respect to different types of possible CTD configurations. In general case of g-As<sub>2</sub>S<sub>3</sub>, the V<sub>1</sub> state corresponds to (As<sub>2</sub><sup>+</sup>;S<sub>1</sub><sup>-</sup>) CP, V<sub>2</sub> state corresponds to (As<sub>4</sub><sup>+</sup>;S<sub>1</sub><sup>-</sup>) CP and W state corresponds to (As<sub>4</sub><sup>+</sup>;S<sub>1</sub><sup>-</sup>) RP.



**Figure 3.** Configuration-coordinate model describing CTD-related metastabilities in g-As<sub>2</sub>S<sub>3</sub>.

Because CTD in V<sub>1</sub> state have very short lifetimes, the following transitions become possible: if  $\Delta E_{V_1B} \geq \Delta E_{V_1A} \approx kT$ , the (As<sub>2</sub><sup>+</sup>;S<sub>1</sub><sup>-</sup>) CP transforms towards A point into V<sub>2</sub> or X state; if  $\Delta E_{V_1B} \ll \Delta E_{V_1A} \approx kT$ , the (As<sub>2</sub><sup>+</sup>;S<sub>1</sub><sup>-</sup>) CP turns back through B point into U state. In both cases, the destroyed covalent bond will renew, and corresponding relaxation process attains a monomolecular (threshold-type) behavior. The V<sub>2</sub> state correspondingly decays through A point into initial X state or,

alternatively, into W state, provided  $\Delta E_{V_2A} \approx \Delta E_{V_2W} \approx kT$ . In the first case, the inverse As–As  $\rightarrow$  As–S bond-changing switching followed by spontaneous  $(As_4^+; S_1^-)$  CP annihilation occurs, while in the second case the bond-conserving As–S  $\rightarrow$  As–As switching followed by  $(As_4^+; S_1^-)$  RP appearance takes place, the both processes being described by bimolecular relaxation kinetics.

It should be noted that CTD-related processes in g-As<sub>2</sub>S<sub>3</sub>-Sb<sub>2</sub>S<sub>3</sub> were exemplified by ones character only for stoichiometric g-As<sub>2</sub>S<sub>3</sub>. In fact, this is not a significant limiting factor, since the corresponding in-put of similar processes in Sb<sub>2</sub>S<sub>3</sub>-based sub-system is relatively small owing to instability of CTD localized on Sb atoms (due to significant decrease in electron correlation energy for corresponding defect pairs) [3]. In other words, the Sb<sub>2</sub>S<sub>3</sub> content in ChG within quasibinary g-As<sub>2</sub>S<sub>3</sub>-Sb<sub>2</sub>S<sub>3</sub> system determines only the weakening in radiation-induced CTD formation.

#### 4. Conclusion

The post-irradiation relaxation in g-(As<sub>2</sub>S<sub>3</sub>)<sub>1-x</sub>(Sb<sub>2</sub>S<sub>3</sub>)<sub>x</sub> attains an activation exponential character owing to spontaneous renovation of destroyed covalent chemical bonds. The corresponding relaxation times are only slightly modified with glass composition, being quite close to a few days, which is supposed to be associated with radiation defects only in As-based sub-matrix. The observed post-irradiation interplay in defect content is described within universal configuration-coordinate model of initial and externally-induced metastabilities in ChG.

#### Acknowledgments

This work was partially supported by Science and Technology Center in Ukraine under regular projects # 3745 and 4418.

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