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Modified correlation equation in the FSDP-related void-based model for $\text{As}_2\text{S}(\text{Se})_3$ chalcogenide glasses

T.S. Kavetskyy

Ivan Franko Drohobych State Pedagogical University, Solid-State Microelectronics Laboratory, 24, I. Franko str., 82100 Drohobych, Ukraine

Abstract. Revised in this work is the correlation equation $Q_1 = 2.3 \times \pi/D$ in the FSDP-related void-based model for $\text{As}_2\text{S}(\text{Se})_3$ chalcogenide glasses between the first sharp diffraction peak (FSDP) position, Q_1 , and nanovoid diameter, D , are modified to be presented in the form of $Q_1 = 1.75 \times \pi/D$, taking into account a newly deduced formula for positron lifetime, τ_2 , versus void radius, R . It is valid for those molecular substrates for R up to 5 Å and when no orthopositronium (*o*-Ps) or very small fractions of *o*-Ps components are observed in positron annihilation lifetime spectroscopy.

Keywords: chalcogenide glass, first sharp diffraction peak, positron annihilation, voids.

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Recently, nanoscale void-species structure has been studied [1, 2] in the As_2Se_3 glass using combination of X-ray diffraction in respect to the first sharp diffraction peak (FSDP-related XRD), treated within a void-based model [3-5], and positron annihilation lifetime spectroscopy (PALS), analyzed within the two-state positron trapping model [6-8]. Assuming that the same nanovoids are responsible for both FSDP and PALS data in terms of Jensen *et al.* [9], the analytical correlation relationship between the FSDP position, Q_1 , and nanovoid diameter, D , has been presented as [1, 2]

$$Q_1 = 2.3 \times \pi/D. \quad (1)$$

In the further work [10], it was shown using the examples of both $\text{g-As}_2\text{Se}_3$ and $\text{g-As}_2\text{S}_3$ (g-glassy) that the analytically found Eq. (1) seems to be similar to the relationship $Q_1 = 2.5 \times \pi/r$, reported by Gaskell [11] and/or Ehrenfest's formula $1.23 = Q_1 r/2\pi$ reported by Rachek [12], where r is a characteristic distance that corresponds to the inter-atomic correlations detected from the pair distribution function, $G(r)$.

The Monte-Carlo simulation results for $\text{g-As}_2\text{Se}_3$ [13, 14] and $\text{g-As}_2\text{S}_3$ [15] have also been applied to confirm the validity of Eq. (1) for these chalcogenides.

Basically, the Eq. (1) comes from the Elliott interpretation [3-5] of nature of the anomalous first sharp diffraction peak (FSDP) as a chemical-order prepeak in the concentration-concentration structure factor, arising from the clustering of interstitial nanovoids around cation-based structural units, tested for AX_2 -type glassy-like materials (e.g. $\text{GeS}(\text{Se})_2$), and resulting in the empirical relationship between the position of the FSDP, Q_1 , and atom-void separation like to diameter of nanovoids, D :

$$Q_1 = 3\pi/2D. \quad (2)$$

If Eq. (2) is presented through a coefficient k , depending on the type of glass structure, the Elliott formula may be written as

$$Q_1 = k \times \pi/D, \quad (3)$$

where $k = 1.5$ for tetravalent AX_2 -type glasses.

To find a correlation equation in the case of pyramidal type $\text{As}_2\text{S}(\text{Se})_3$ glasses, the Jensen *et al.* [9] regularity between the positron lifetime, τ (in ns), and vacancy volume, V (in Å³), has been applied [1, 2] in the form of expression:

$$\tau \cong 0.240 + 0.0013 \times V. \quad (4)$$

Recently, Liao *et al.* [16] reported a newly modified positron lifetime-free volume correlation equation for determination of free volumes up to the mean radius $R = 5 \text{ \AA}$ in polymeric systems, where no orthopositronium (*o*-Ps) ($\tau_3 = 1...4 \text{ ns}$) or very small fractions of *o*-Ps components are observed in PALS, which is based on the infinitive potential spherical model (originally proposed by Tao [17]) and presented as

$$\tau_2 = 0.260 \times [1 - (R/(R + 3.823)) + 1/2\pi \times \sin(2\pi R/(R + 3.823))]^{-1}. \quad (5)$$

For simplicity, it was shown in [16] that $\tau_2 - R$ correlation for $R < 5 \text{ \AA}$ could be approximated and empirically fitted by a linear equation as

$$\tau_2 = 0.174(1 + 0.494R), \quad (6)$$

where τ_2 and R are expressed in the units of nanoseconds and angstroms, respectively.

As chalcogenide glasses in their chemical nature are covalent disordered inorganic polymers [18], and, in respect to positron annihilation, they should be considered as inorganic polymers without *o*-Ps component or with very small fraction of *o*-Ps component in PALS (see, for example, [8, 19, 20]), the Liao *et al.* correlation equations (5) and/or (6) are valid in the first approximation for these materials and can be used obviously for $\text{As}_2\text{S}(\text{Se})_3$ alloys.

The values of void radius R or void volume V ($V = 4/3 \times \pi R^3$) estimated using positron lifetime-free volume correlation equations are given in Table. As seen, the difference between values of V calculated from Eqs. (5) and (6) is $\sim 15 \text{ \AA}^3$, which is rather small to be affected on the average size of voids, whereas the void volume V calculated from Eq. (4) is larger by 30 to 50 \AA^3 .

Liao *et al.* [16] noted that Eq.(5) should be applied for $\tau_2 \approx 0.35$ to 0.40 ns , while for the shortest $\tau_2 < 0.26 \text{ ns}$ this equation is not applicable, while the linear Eq. (6) works better. It is noticeable that the correlation coefficients ($r^2 = 0.9391$) for Eq. (5) and ($r^2 = 0.9268$) for Eq. (6) are very similar [16], and, thus, it is suggested that the linear equation could be also used

in more general cases for $\tau_2 \approx 0.35$ to 0.40 ns when various polymeric materials (organic and inorganic) are examined. Taking into account that Eq. (5) is deduced by Liao *et al.* [16] using the example of organic polymers having preferential hydrocarbon environment, while chalcogenide glasses are inorganic polymers, the linear Eq. (6) is applied in the present work.

The values of the open-volume defect-related positron lifetime component τ_2 are known to be 0.37 ns for $\text{g-As}_2\text{Se}_3$ [21] and 0.36 ns for $\text{g-As}_2\text{S}_3$ [22]. According to Eq. (6), the values of void radius R are 2.28 \AA ($D = 4.6 \text{ \AA}$) for $\text{g-As}_2\text{Se}_3$ and 2.16 \AA ($D = 4.3 \text{ \AA}$) for $\text{g-As}_2\text{S}_3$. The values of the FSDP position Q_1 are known to be 1.25 \AA^{-1} for $\text{g-As}_2\text{Se}_3$ and 1.26 \AA^{-1} for $\text{g-As}_2\text{S}_3$ (see, for example [1, 2, 10, 23] and references therein). Thus, corresponding to Eq. (3), the values of the coefficient k are obtained to be 1.8 for $\text{g-As}_2\text{Se}_3$ and 1.7 for $\text{g-As}_2\text{S}_3$. In average, for pyramidal-type $\text{As}_2\text{S}(\text{Se})_3$ glasses, the value of the coefficient k is 1.75 and modified correlation equation in the FSDP-related void-based model for these alloys can be written as

$$Q_1 = 1.75 \times \pi/D. \quad (7)$$

Therefore, using the newly modified positron lifetime-free volume correlation equation, Eq. (6), it is found that the established value of $k = 1.75$ for pyramidal type $\text{As}_2\text{S}(\text{Se})_3$ glasses is very close to the above mentioned Elliott's value of $k = 1.5$ for tetravalent AX_2 -type glasses. On the basis of this similarity in k values, it is suggested that the nature of the FSDP for pyramidal-type $\text{As}_2\text{S}(\text{Se})_3$ glasses and tetravalent AX_2 -type glasses (e.g., $\text{A} = \text{Ge}$, $\text{X} = \text{S}, \text{Se}$) is the same or very similar. In other words, in terms of the FSDP-related void-based model [3-5], the cation-centered nanovoids with the same or very similar size are responsible for the FSDP occurrence in the both pyramidal and tetrahedral type chalcogenide glasses. This finding gives a new insight on the explanation of experimental observation that the FSDP position in the mixed pyramidal-tetrahedral type chalcogenide glasses, such as $\text{As}(\text{Sb})_2\text{S}_3\text{-GeS}_2$ and $\text{As}(\text{Sb})_2\text{S}_3\text{-Ge}_2\text{S}_3$, is determined exclusively by concentration of Ge cations, while As and Sb cations do not affect the FSDP

Table. The values of positron lifetime τ_2 as typical for chalcogenide glasses as well as the void radius R and void volume V calculated from Eqs. (4) to (6).

τ_2 (ns)	0.35	0.36	0.37	0.38	0.39	0.40	0.41
Jensen's <i>et al.</i> approach, Eq.(4)							
R (\AA)	2.73	2.80	2.88	2.95	3.02	3.08	3.15
V (\AA^3)	85	92	100	108	115	123	131
Liao's <i>et al.</i> approach, Eq.(5)							
R (\AA)	2.26	2.40	2.50	2.60	2.71	2.81	2.91
V (\AA^3)	48	58	65	74	83	93	103
Liao's <i>et al.</i> approach, Eq.(6)							
R (\AA)	2.05	2.16	2.28	2.40	2.51	2.63	2.75
V (\AA^3)	36	42	50	58	66	76	87

occurrence [23, 24]. The most probably it is caused by the similar size of cation-centered nanovoids in the pyramidal and tetrahedral type chalcogenide glasses.

From this viewpoint, the previously used Jensen *et al.* [9] theoretical calculations of positron annihilation lifetime versus open volume in application to chalcogenide glasses should be modified (see Eq. (4)). One of the reasons for this required modification can be a suggestion based on the two-component electron-positron density functional theoretical calculations [25, 26] that a symmetric fourfold tetravacancies formed during the clustering process have the positron lifetime similar to that of divacancies, and fourfold trivacancies have the positron lifetime similar to that of monovacancies. This suggestion shows the possible confusion in the interpretation of positron annihilation lifetime data and explains why the conclusion made using Eq. (4) [23] that the size of nanovoids changes from three atomic vacancies for pyramidal type chalcogenide glasses to di- and/or monovacancies for tetrahedral type and pyramidal-tetrahedral type chalcogenide glasses should be reconsidered.

Finally, on the basis of the modified correlation equation, Eq. (7), reported here, it is easy to calculate that the size of nanovoids in the pyramidal type $As_2S(Se)_3$ glasses with average value of radius $R \cong 2.22 \text{ \AA}$ (or volume $V \cong 46 \text{ \AA}^3$) corresponds to the size of di- and/or monovacancies similarly to the size of nanovoids in the tetrahedral type $GeS(Se)_2$ glasses [23] and mixture of pyramidal and tetrahedral structural units in chalcogenide glassy network should not practically affect the size of nanovoids responsible for the FSDP occurrence within the FSDP-related void-based model [3-5], as it is indeed experimentally observed [23, 24]. This agreement between calculation and experimental results may be also considered for validity of linear Eq. (6) to be applied for $\tau_2 \approx 0.35$ to 0.40 ns in the case of inorganic polymers like to chalcogenide glasses.

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