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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

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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., $\text{A} = \text{Ge}$, $\text{X} = \text{S}$, 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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References

1. T.S. Kavetskyy, O.I. Shpotyuk, Nanostructural voids in glassy-like As_2Se_3 studied with FSDP-related XRD and PALS techniques // *J. Optoelectron. Adv. Mater.*, **7**(5), p. 2267-2273 (2005).
2. O. Shpotyuk, A. Kozdras, T. Kavetskyy, J. Filipecki, On the correlation between void-species structure of vitreous arsenic selenide studied with X-ray diffraction and positron annihilation techniques // *J. Non-Cryst. Solids*, **352**, p. 700-703 (2006).
3. S.R. Elliott, Origin of the first sharp diffraction peak in covalent glasses // *Phys. Rev. Lett.*, **67**(6), p. 711-714 (1991).
4. S.R. Elliott, Medium-range structural order in covalent amorphous solids // *Nature*, **354**, p. 445-452 (1991).
5. S.R. Elliott, Extended-range order, interstitial voids and the first sharp diffraction peak of network glasses // *J. Non-Cryst. Solids*, **182**, p. 40-48 (1995).
6. P. Hautojarvi, C. Corbel, Positron spectroscopy of defects in metals and semiconductors // *In: Positron Spectroscopy of Solids, Proc. the Intern. School of Physics "Enrico Fermi", Course CXXV ed. by A. Dupasquier, A.P. Mills jr. (Villa Monastero, Italy, 6-16 July 1993)*, Amsterdam, Oxford, Tokyo, Washington DC, IOS Press, p. 491-532 (1995).
7. R. Krause-Rehberg, H.S. Leipner, *Positron Annihilation in Semiconductors. Defect Studies*. Berlin, Heidelberg, New York, Springer-Verlag, 1999.
8. O. Shpotyuk, J. Filipecki, *Free Volume in Vitreous Chalcogenide Semiconductors: Possibilities of Positron Annihilation Lifetime Study*. Czestochowa, WSP w Czestochowie (2003).
9. K.O. Jensen, P.S. Salmon, I.T. Penfold, P.G. Coleman, Microvoids in chalcogenide glasses studied by positron annihilation // *J. Non-Cryst. Solids*, **170**, p. 57-64 (1994).
10. T.S. Kavetskyy, O.I. Shpotyuk, V.T. Boyko, Void-species nanostructure in chalcogenide glasses studied with FSDP-related XRD // *J. Phys. Chem. Solids*, **68**, p. 712-715 (2007).
11. P.H. Gaskell, Medium-range structure in glasses and low- Q structure in neutron and X-ray scattering data // *J. Non-Cryst. Solids*, **351**, p. 1003-1013 (2005).
12. O.P. Rachek, X-ray diffraction study of amorphous alloys Al-Ni-Ce-Sc with using Ehrenfest's formula // *J. Non-Cryst. Solids*, **352**, p. 3781-3786 (2006).
13. M.A. Popescu, Hole structure of computer models of non-crystalline materials // *J. Non-Cryst. Solids*, **35-36**, p. 549-554 (1980).
14. O. Shpotyuk, A. Kovalskiy, J. Filipecki, T. Kavetskyy, M. Popescu, Positron annihilation lifetime spectroscopy as experimental probe of free volume concepts in network glasses // *Phys. Chem. Glasses: Eur. J. Glass. Sci. Technol. B*, **47**(2), p. 131-135 (2006).
15. T. Kavetskyy, O. Shpotyuk, V. Boyko, J. Filipecki, M. Popescu, On the origin of nanovoids in binary chalcogenide glasses studied by FSDP-related XRD, PALS and Monte-Carlo simulation // *Visnyk Lviv Univ., Ser. Physics*, **40**, p. 153-158 (2007).
16. Kuo-Sung Liao, Hongmin Chen, Somia Awad, Jen-Pwu Yuan, Wei-Song Hung, Kuier-Rarn Lee, Juin-Yih Lai, Chien-Chieh Hu, Y.C. Jean, Determination of free-volume properties in polymers without orthopositronium components in positron annihilation lifetime spectroscopy // *Macromolecules*, **44**(17), p. 6818-6826 (2011).

17. S.J. Tao, Positronium annihilation in molecular substances // *J. Chem. Phys.*, **56**(11), p. 5499-5510 (1972).
18. A. Saiter, J-M. Saiter, R. Golovchak, M. Shpotyuk, O. Shpotyuk, Cooperative rearranging region size and free volume in As-Se glasses // *J. Phys.: Condens. Matter*, **21**(7), 075105 (2009).
19. M. Singh, Y.K. Vijay, I.P. Jain, Y.S. Shishodia, Study of AsGeSe structures by positron lifetime technique // *J. Non-Cryst. Solids*, **93**, p. 273-276 (1987).
20. T.S. Kavetsky, O. Šauša, V.F. Valeev, V.I. Nuzhdin, N.M. Lyadov, A.L. Stepanov, Raman, positron annihilation and Doppler broadening spectroscopy of gamma-irradiated and Cu-ion implanted $\text{Ge}_{15.8}\text{As}_{21}\text{S}_{63.2}$ glass // *In book: Coherent Optics and Optical Spectroscopy: XV Intern. junior sci. school 24-26 October 2011*, ed. by M.Kh. Salakhov, Kazan, Kazan Univ., **15**, p. 86-89 (2011).
21. A. Kozdras, J. Filipecki, M. Hyla, O. Shpotyuk, A. Kovalskiy, S. Szymura, Nanovolume positron traps in glassy-like As_2Se_3 // *J. Non-Cryst. Solids*, **351**, p. 1077-1081 (2005).
22. T. Kavetsky, J. Borc, P. Petkov, K. Kolev, T. Petkova, Free-volume defects and microstructure in ion-conducting $\text{Ag}/\text{AgI}-\text{As}_2\text{S}_3$ glasses as revealed from positron annihilation and microhardness measurements // *Solid State Ionics*, **183**, p. 16-19 (2011).
23. T. Kavetsky, O. Shpotyuk, I. Kaban, W. Hoyer, J. Filipecki, Nanostructural characterization of amorphous chalcogenides by X-ray diffraction and positron annihilation techniques // *In book: NATO Science for Peace and Security Series B: Physics and Biophysics, "Nanostructured materials for advanced technological applications"* ed. by J.P. Riethmaier, P. Petkov, W. Kulisch, C. Popov. Berlin, Springer, p. 365-370 (2009).
24. T. Kavetsky, O. Shpotyuk, I. Kaban, W. Hoyer, V. Tsmots, On the origin of the first sharp diffraction peak in chalcogenide glasses // *In book: Bulletin of center of chemotronic of glass named after V.V. Tarasov #4, Reports of scientific session in occasion of 100 years after birthday of Professor B.T. Kolomiets*, Moscow, p. 112-115 (2008), in Russian.
25. D.V. Makhov, L.J. Lewis, Stable four-fold configurations for small vacancy clusters in silicon from *ab initio* calculations // *Phys. Rev. Lett.*, **92**(25), 255504(1-4) (2004).
26. D.V. Makhov, L.J. Lewis, Two-component density functional theory calculations of positron lifetimes for small vacancy clusters in silicon // *Phys. Rev. B*, **71**(20), 205215(1-6) (2005).