

On the concentrations of magnetically ordered clusters and paramagnetic centers per magnetic cluster in Ag/AgI-As₂S₃ glasses

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In the present work the magnetic properties of Ag/AgI-As₂S₃ glasses are studied using magnetic susceptibility (MS) measurement by the Faraday method at the temperatures of 293 and 77 K. On the basis of the MS experimental data and the model based on the Langevin function, the concentrations of magnetically ordered clusters and paramagnetic centers per magnetic cluster for the investigated glasses are evaluated and the results obtained are discussed.

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1. Introduction

Ionic mobility in chalcogenide glasses is responsible for many applications in different domains such as ion-exchange strengthening, chemical sensors, solid state batteries, the electrochemical storage of energy and waveguides for integrated optical devices [1,2]. Thus, a survey of ionic transport in network glasses is a topic of interest to the academic community as well as to glass industry. Knowledge of the mobile ion dynamics at both macroscopic and atomic levels is needed in order to learn structure and properties in ion-conducting chalcogenide glasses could be linked together. Silver containing chalcogenide glasses are well known due to their potential application in solid state electrochemical devices. Despite extensive studies of ionic transport mechanism in such materials, the structure-property relationship in Ag/AgI-As₂S₃ glasses is rather not well understood yet that is very important to improve their applications.

Recently, it has been found in the case of (As₂S₃)₈₅Ag₁₅ glass [3,4] that the hole-like defects with volume about 18-20 Å³ occupied by the Ag⁺ ions are present in the structure of the host glass matrix As₂S₃. This finding enables the authors to consider that because of disorder, it is possible to assume the existence of 'dangling' or 'broken' bonds, which allows the easy migration of Ag as ions in the random constructed glass matrix. The dangling bonds or paramagnetic centers should form magnetically ordered clusters in the material, which can be evaluated in terms of the model based on the

Langevin function [5]. Recently, such approach has been applied for the γ -radiation-modified As₂S₃ and Ge_{28.125}As_{6.250}S_{65.625} chalcogenide glasses [6]. The goal of this work is to evaluate the concentrations of magnetically ordered clusters and paramagnetic centers per magnetic cluster in Ag/AgI-As₂S₃ glasses on the basis of the experimental results obtained using magnetic susceptibility (MS) measurements by the Faraday method at the temperatures of 293 and 77 K and the model based on the Langevin function.

2. Experimental

The samples were prepared in evacuated ($\sim 10^{-3}$ Pa) and sealed quartz ampoules by a conventional direct monotemperature synthesis in a rotary furnace. The procedure of samples preparation consists of two stages: i) synthesis of binary As₂S₃ glass from the initial elements As with a purity of 5N and S (5N), products of Alfa Aesar company, ii) preparation of the pseudo-binary and ternary samples by mixing As₂S₃ with additives of Ag or AgI the respective amount of 5-25 mol.%. Stepwise heating regimes were employed with temperature maintenance at the melting temperatures of the components for 2 hours and vibrational stirring at higher temperatures. The final temperature of synthesis (1200 K) was kept for 2 hours and followed by rapid quenching in the mixture of water and ice. The following glass compositions of Ag/AgI-As₂S₃ systems are used for measurements: As₂S₃,

(As₂S₃)₉₅Ag₅, (As₂S₃)₇₅Ag₂₅, (As₂S₃)₉₅(AgI)₅, and (As₂S₃)₈₅(AgI)₁₅. The evaluation of concentrations of magnetically ordered clusters and paramagnetic centers per magnetic cluster in the As₂S₃ glass has already been done in [6].

The MS experiments were performed using equipment for measurements of weak magnetic materials by the Faraday method. The advantage of this technique is possibility to measure the samples with optimal mass and length of 120-150 mg and 8-10 mm, respectively. The main parameters of the equipment for the MS measurements were: diameter of quartz capillary 0.5 mm; its length 950 mm; distance from sample to axis of quartz capillary 12 mm; and own frequency of torque balance without sample 140 Hz. The experiments were carried out at the temperatures of 293 and 77 K in the magnetic field range of 0.3-5.0 kOe. The automatized equipment by removing the error of the MS measurement connected with deformation of current supplies due to adding the new assemblies of control, i.e., device with comparator, were used [7]. In this way, the accuracy of experimental data was essentially increased, giving the relative error to be less than 1%, and the sensitivity to be 5·10¹⁵ Bohr magnetons.

3. Results and discussion

Detected dependences of the MS χ on the external magnetic field strength H of the investigated glasses at $T = 293$ K and 77 K are plotted in Fig. 1 (data for As₂S₃ are taken from [6]). One can see that the $\chi(H)$ curves are not linear for the all samples. Such $\chi(H)$ behavior can be considered as the sum of two components, one independent on H (χ^{ind}) and another is a function of H ($\chi^{\text{ord}}(H)$), which is associated with ordering of magnetic centers in the glass matrix [5],

$$\chi(H) = \chi^{\text{ind}} + \chi^{\text{ord}}(H). \quad (1)$$

The component χ^{ind} corresponds to the MS saturation value, which is more or less attained in the samples studied in the range of magnetic fields of 3-4 kOe. In general [5], the component χ^{ind} consists of two other ones – the lattice susceptibility χ_L (see [8] for details on χ_L for chalcogenide glasses) and the paramagnetic component χ^{par} independent on H ,

$$\chi^{\text{ind}} = \chi_L + \chi^{\text{par}}. \quad (2)$$

The decrease in diamagnetism of the all samples at the temperature 77 K is due to the increase in the paramagnetism χ^{par} and $\chi^{\text{ord}}(H)$. The χ^{par} is probably caused by the dispersed paramagnetic centers existing in the glass matrix as dangling bonds, while the $\chi^{\text{ord}}(H)$ is dependent on H in the whole range of 0-5 kOe. In relation to behavior of $\chi^{\text{ord}}(H)$, one can consider the paramagnetism connected with appearance of magnetically ordered clusters, the susceptibility of which

is similar to Langevin approach to atoms with magnetic moments. It is noteworthy here that the magnetic moment of such magnetically ordered clusters could be significantly larger (by a factor of 10³-10⁵) than the magnetic moment of isolated atoms [5].

In order to evaluate the concentrations of magnetically ordered clusters and paramagnetic centers per magnetic cluster the model based on the Langevin function can be applied similarly as reported in [5]. In this model the dependence $\chi(H)$ is presented by relation

$$\chi(H) = \chi_L + \chi^{\text{par}} + \chi^{\text{ord}}(H) = \chi_L + \chi^{\text{par}} + N_{\text{cl}} m_{\text{cl}} L'(m_{\text{cl}} H/kT), \quad (3)$$

where N_{cl} is the concentration of magnetically ordered clusters, m_{cl} is magnetic moment of the cluster (in a first approximation, it is suggested that all the clusters have identical magnetic moment), and $L'(x)$ is the derivative of the Langevin function ($L = (\coth \alpha - 1/\alpha)$, where $\alpha = MH/kT$, M is the magnetization, k is the Boltzmann constant, and T is the temperature). Magnetic moment of the cluster follows the expression [5]

$$m_{\text{cl}} = N_0 \mu_B g(s(s+1))^{1/2}, \quad (4)$$

where N_0 is the concentration of paramagnetic centers per magnetic cluster, μ_B is the Bohr magneton, g is the g -factor and s is the spin of paramagnetic center composing the magnetic cluster. Finally, the $\chi(H)$ can be written as

$$\chi(H) = \chi_L + \chi^{\text{par}} + N_{\text{cl}} N_0 \mu_B g(s(s+1))^{1/2} L'(N_0 \mu_B g(s(s+1))^{1/2} H/kT). \quad (5)$$

Smith [9] reported on a single, dipolar broadened line at $g \cong 2.0055$ with a width of approximately 2 gauss for the most samples of As₂S₃-based chalcogenide glasses. Bishop and Taylor [10] showed that the optically induced ESR signals in As₂S₃ glass observed near $g = 2$ are insensitive to the incorporation of various dopants and to the application of near-band gap light. Thus, the values of $g = 2$ and electron spin $s = 1/2$ are taken for estimations in the present work.

The approximations of the experimental dependences $\chi(H)$ by expression (5) for the investigated glasses are shown in Fig. 2 (see Ref. [6] for As₂S₃). The N_{cl} and N_0 parameters obtained from the simulations performed are presented in Table 1.

It is seen that the values of N_{cl} and N_0 are found to be comparable between the As₂S₃, (As₂S₃)₇₅Ag₂₅, and (As₂S₃)₈₅(AgI)₁₅ with $N_{\text{cl}} \times N_0$ of the order of 10¹⁷ cm⁻³ and between the (As₂S₃)₉₅Ag₅ and (As₂S₃)₉₅(AgI)₅ with $N_{\text{cl}} \times N_0$ of the order of 10¹⁸ cm⁻³ at $T = 77$ K. Such peculiarities are not seen at $T = 293$ K, but it is well known that the paramagnetic centers are better detectable at low temperature. It should be noted that the magnitude of $N_{\text{cl}} \times N_0$ of the order of 10¹⁷-10¹⁸ cm⁻³ is in the frame of the concentrations 10¹²-10²⁰ cm⁻³ of intrinsic, photoinduced, and impurity paramagnetic centers in chalcogenide glasses deduced by EPR [11-13].

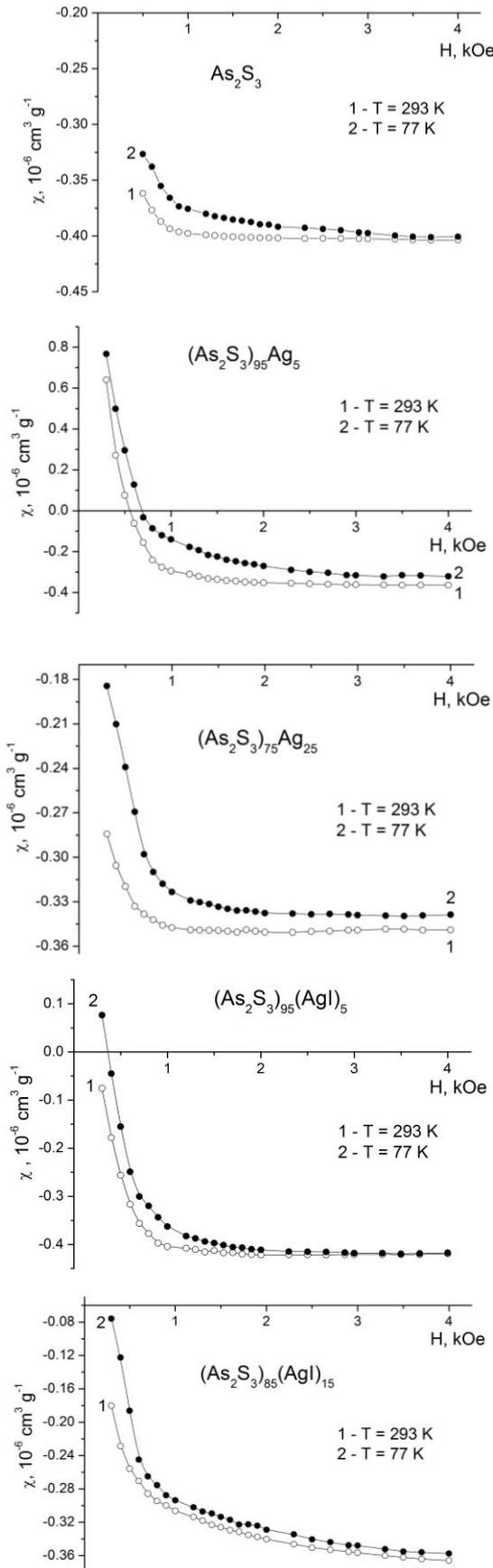


Fig. 1. Dependences of the magnetic susceptibility χ on the external magnetic field strength H for the investigated glasses at $T = 293$ K and $T = 77$ K.

Thus, we found that the addition of 5 at.% Ag and/or 5 mol.% (AgI) within the Ag-As₂S₃ and AgI-As₂S₃ glassy systems results in increasing in the values of N_{cl} and N_0 , giving the magnitude of $N_{cl} \times N_0$ of the order of 10^{18} cm⁻³ at $T = 77$ K, while the addition of 25 at.% Ag and/or 15 mol.% (AgI) within these systems shows opposite effect leading to practically the same values of N_{cl} and N_0 as for the As₂S₃ glass, giving the magnitude of $N_{cl} \times N_0$ of the order of 10^{17} cm⁻³ at $T = 77$ K. These findings could be explained by closing of dangling bonds with increasing of Ag and/or AgI amount in the glass host, resulting in decreased magnitude of $N_{cl} \times N_0$ by a factor of 10. A good correlation between MS data in terms of N_{cl} and N_0 and EPR data, reported for the γ -radiation-modified As₂S₃ glass [6], supports these observations.

The results obtained on the peculiarities in the values of N_{cl} and N_0 are in consistence with the structural data reported in literature. For instance, using high-energy X-ray diffraction, neutron diffraction, extended X-ray absorption fine structure spectroscopy and reverse Monte-Carlo simulation, Kaban *et al.* [14] showed that addition of Ag to As₂S₃ within ternary (As_{0.4}S_{0.6})_{100-x}Ag_x ($x = 0, 4, 8, 12$ at.%) glass system mainly results in the formation of Ag-S and As-As bonds; and a small portion of Ag-As bonds is also formed upon the addition of Ag, but the direct Ag-Ag bonds appear only in the glass composition with the highest Ag content (12 at.%). Although the authors [14] noted that the addition of Ag does not change the mean coordination number of As (~ 3.0) and S (~ 2.0), it is assumed that due to appearance of Ag-S and As-As bonds instead of As-S ones the paramagnetic centers or dangling bonds may be occurred for the (As₂S₃)₉₅Ag₅ glass, taking into account that the concentration of atomic sites of the order of 10^{17} - 10^{18} cm⁻³ is far below a detection limit of X-ray diffraction [15]. When amount of Ag in As₂S₃ binary increases up to 25 at.%, a portion of direct Ag-Ag bonds would be also increased. Thus, both the Ag-S and Ag-Ag correlations may interact with dangling bonds resulting in decreased magnitude of $N_{cl} \times N_0$ for the (As₂S₃)₇₅Ag₂₅ glass.

At the same time, the similar structure as for glasses of AgI-As₂Se₃ system, which is proposed to be a pseudo-binary mixture of AsSe_{3/2} network matrix and dispersed AgI clusters [16], is suggested for glasses of AgI-As₂S₃ system. This suggestion is also supported by the results of ¹⁰⁹Ag NMR study of the (As₂S₃)₆₅(AgI)₃₅ glass [17], showing the chemical shift measured on the sample happens to be identical to that in α - and β -AgI [18] and giving therefore a good indication that AgI clusters occur and AgI does not act as a network modifier. In this case it is assumed that: (i) when the amount of AgI in As₂S₃ binary is small (5 mol.%) the AgI clusters are dispersed more randomly and paramagnetic centers or dangling bonds are appeared for the (As₂S₃)₉₅(AgI)₅ glass; (ii) but for larger amount of AgI (15 mol.%) the AgI clusters are dispersed more compact in the glass backbone and the interaction between AgI clusters and dangling bonds may exist resulting in decreased magnitude of $N_{cl} \times N_0$ for the (As₂S₃)₈₅(AgI)₁₅ glass.

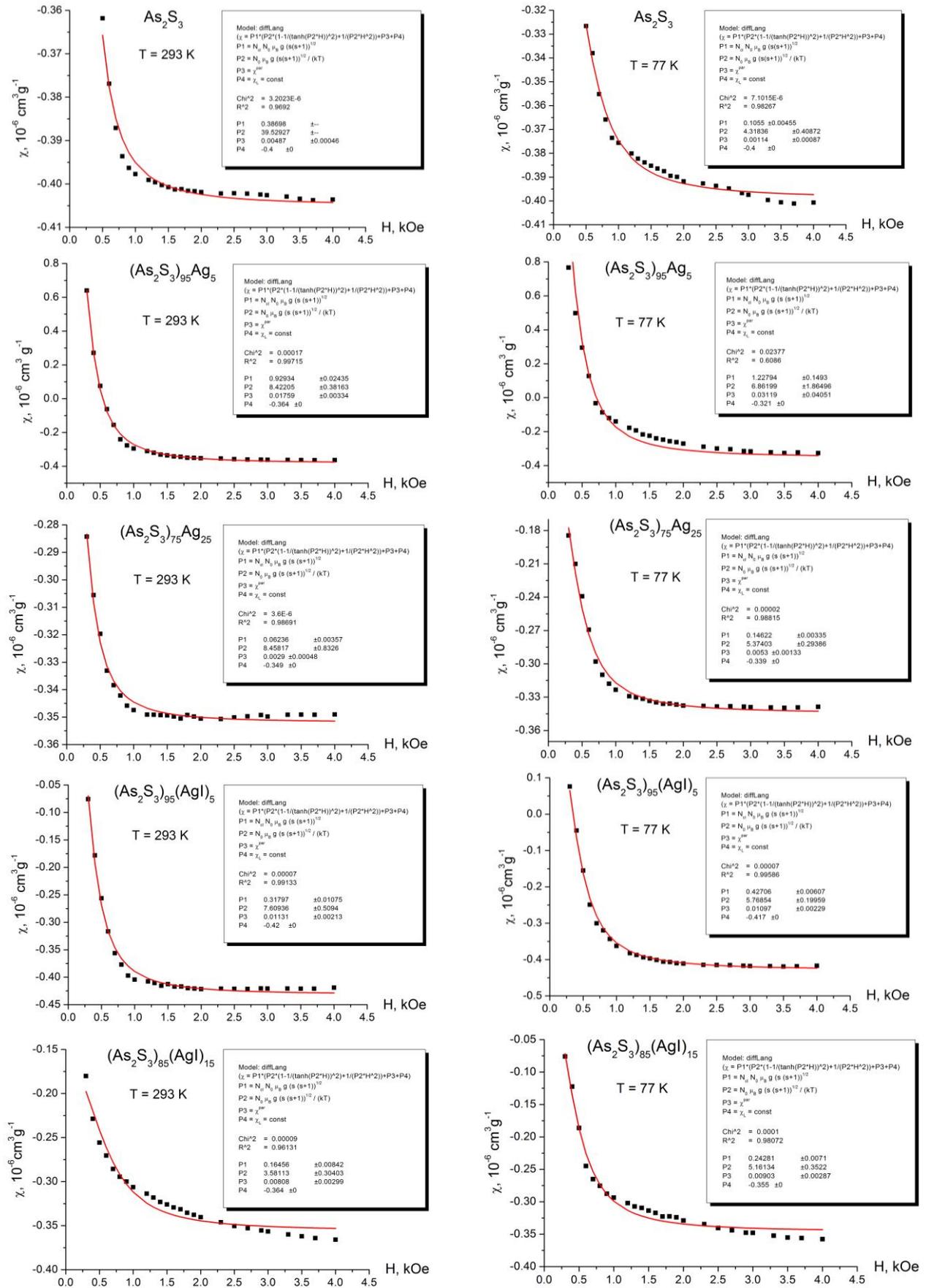


Fig. 2. Approximations of the experimental dependences $\chi(H)$ by expression (5) for the investigated glasses at $T = 293 \text{ K}$ (left) and $T = 77 \text{ K}$ (right).

Table 1. The evaluated concentrations of magnetically ordered clusters N_{cl} and paramagnetic centers per magnetic cluster N_0 for the investigated glasses at $T = 293$ K and $T = 77$ K.

[*] As ₂ S ₃	293 K	77 K
N_{cl}, cm^{-3}	2.4×10^{11}	2.3×10^{12}
$N_0, \text{1/cluster}$	936.9×10^5	28.6×10^5
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(As ₂ S ₃) ₉₅ Ag ₅	293 K	77 K
N_{cl}, cm^{-3}	2.7×10^{12}	1.7×10^{13}
$N_0, \text{1/cluster}$	212.2×10^5	45.5×10^5
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(As ₂ S ₃) ₇₅ Ag ₂₅	293 K	77 K
N_{cl}, cm^{-3}	1.8×10^{11}	2.6×10^{12}
$N_0, \text{1/cluster}$	213.2×10^5	35.6×10^5
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(As ₂ S ₃) ₉₅ (AgI) ₅	293 K	77 K
N_{cl}, cm^{-3}	1.0×10^{12}	6.9×10^{13}
$N_0, \text{1/cluster}$	191.9×10^5	38.2×10^5
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(As ₂ S ₃) ₈₅ (AgI) ₁₅	293 K	77 K
N_{cl}, cm^{-3}	1.1×10^{12}	4.4×10^{12}
$N_0, \text{1/cluster}$	90.2×10^5	34.2×10^5

* - the data of Tsmots *et al.* [6].

4. Conclusions

The magnetic properties of the Ag/AgI-As₂S₃ glasses have been studied using MS measurements by Faraday method at the temperatures of 293 and 77 K. On the basis of the experimental data and the model based on the Langevin function, the concentrations of magnetically ordered clusters N_{cl} and paramagnetic centers per magnetic cluster N_0 for the Ag/AgI-containing glasses have been evaluated. The peculiarities in the values of N_{cl} and N_0 have been found at low temperature. It has been established that the magnitude of $N_{cl} \times N_0$ increases with addition of small amount of Ag (5 at.%) and/or AgI (5 mol.%) to As₂S₃ binary and decreases by a factor of 10 when larger amount of Ag (25 at.%) and AgI (15 mol.%) is added to As₂S₃ binary. These findings could be explained by interaction of Ag-S and Ag-Ag correlations and/or AgI clusters with dangling bonds with increasing of Ag and/or AgI amount in the glass host.

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References

- [1] A. Piarristeguy, M. Ramonda, N. Frolet, M. Ribes, A. Pradel, *Solid State Ionics* **181**, 1205 (2010).
- [2] A. Pradel, N. Kuwata, M. Ribes, *J. Phys.: Condens. Matter* **15**, S1561 (2003).
- [3] T. Kavetsky, J. Borc, P. Petkov, K. Kolev, T. Petkova, V. Tsmots, *Solid State Ionics* **233**, 107 (2013).
- [4] T. Kavetsky, J. Borc, P. Petkov, K. Kolev, T. Petkova, *Solid State Ionics* **183**, 16 (2011).
- [5] V. M. Tsmots, P. G. Litovchenko, N. T. Pavlovskaya, Yu. V. Pavlovskyy, I. P. Ostrovskyy, *Semiconductors* **44**(5), 623 (2010).
- [6] V. M. Tsmots, T. S. Kavetsky, L. I. Pankiv, *Urgent Problems of Physics, Mathematics and Computer Sciences* **3**, 16 (2011), in Ukrainian.
- [7] V. M. Tsmots, I. S. Pankiv, L. I. Pankiv, Yu. V. Pavlovskyy, V. V. Petrenko, T. S. Kavetsky, D. V. Labovka, M. M. Luchkevych, R. V. Okhrymovych, V. P. Salan, M. V. Tsyuper, Patent of Ukraine, **77284**, 15.11.2006.
- [8] M. A. Popescu, *Non-Crystalline Chalcogenides*, Kluwer Academic Publishers, Dordrecht, 2000.
- [9] R. E. Smith, *J. Non-Cryst. Solids* **8-10**, 598 (1972).
- [10] S. G. Bishop, P. C. Taylor, *Philos. Mag. B* **40**(6), 483 (1979) (and references therein).
- [11] I. V. Chepeleva, *J. Non-Cryst. Solids* **97-98**, 1179 (1987).
- [12] E. A. Zhilinskaya, V. N. Lazukin, N. Kh. Valeev, A. K. Oblasov, *J. Non-Cryst. Solids* **124**, 48 (1990).
- [13] L. N. Blinov, *Glass Physics and Chemistry* **29**(3), 203 (2003).
- [14] I. Kaban, P. J v ri, T. Wagner, M. Frumar, S. Stehlik, M. Bartos, W. Hoyer, B. Beuneu, M. A. Webb, *J. Phys.: Condens. Matter* **21**, 395801 (2009).
- [15] K. Tanaka, *Semiconductors* **32**(8), 861 (1998).
- [16] T. Usuki, S. Saito, K. Nakajima, O. Uemura, Y. Kameda, T. Kamiyama, M. Sakurai, *J. Non-Cryst. Solids* **312-314**, 570 (2002).
- [17] T. S. Kavetsky, J.-J. Ren, G. Bruncklaus, K. Meise-Gresch, H. Eckert, V. M. Tsmots, T. Petkova, P. Petkov, K. Kolev, A. L. Stepanov, Abstracts of International Meeting "Clusters and Nanostructured Materials (CNM-3'2012)" (Uzhgorod, Ukraine, 14-17 October, 2012), p.178.
- [18] J. Kawamura, N. Kuwata, Y. Nakamura, T. Erata, T. Hattori, *Solid State Ionics* **154-155**, 183 (2002).

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