LOW-FREQUENCIES (LF) RAMAN SPECTRUMS OF As_xS_{1-x} GLASSES, VIBRATIONAL SPECTRUMS OF As_nS_m CLUSTERS CALCULATED BY "AB INITIO" METHOD AND THE DISTRIBUTION OF CLUSTERS LENGTH

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The results of comparison of spectral position of the LF bands of As-S glass system with theoretical calculation of vibrational spectra of different clusters (As_2S_3, As_2S_5, As_4S_6, As_6S_9) in the LF region (5-100 cm^{-1}) are given. Calculated distribution of clusters lengths f(L) for As_2S_3 glass.

I. Introduction

The idea of cluster arrangement of atoms or atomic bonds can be very helpful in understanding the physics of amorphous system. Low-frequency (LF) Raman measurements of amorphous semiconductors (AS) are analyzed in order to find evidence for any possible cluster arrangement of AS. The presence of different vibrational modes in the same frequency range as fractons should also be considered for both theoretical calculations of vibrational spectra of different sizes of clusters and light scattering experiment of amorphous system [1-3]. The aim of this work is comparison of vibration frequencies of clusters with a position of a LF maximum (Boson peak), and also calculation of a distribution function of the ordered lengths of chains.

II. Experiments and data analysis

Right angle Raman spectra were measured with the use of DFS-24 spectrometer. A spectral slit width was 1 cm^{-1}. The polarization of incident light was parallel and that of scattered light was normal to the scattering plain. Excitation laser beam 632,8 nm were used.

The sizes distribution of chain sequences may be calculated in chain approximation on ratio [4]:

$$L_i = \frac{m}{2c\Delta\nu_i}\left(\frac{E_c}{\rho}\right)^{1/2}, \qquad (1)$$

here m is the mode order, c is the speed of light, $\Delta\nu_i$ is the mode frequency, E_c is the Young's modulus, ρ is the density of glass.

Broad size distributions are quite common and under these circumstances ratio (1) cannot be applied directly [5-8] and some authors [9, 10] obtained the relation

$$f(L_i) \propto \left[1-\exp(-\frac{hc\Delta\nu_i}{kt})\right](\Delta\nu_i)^2 I_{\nu_i} \qquad (2)$$

Here I_{ν_i} is the observed scattering intensity at the frequence $\Delta\nu_i$. The factor $\left[1-\exp(-\frac{hc\Delta\nu_i}{kt})\right]$ is an intensity correction for the Boltzmann population of vibrational energy levels. The weighting factor $\Delta\nu_i^{\,2}$ occurs in the equation because of the distribution function $f(L_i)$ is defined for equal increments in L_i, while the spectrum is determined for increments in $\Delta\nu_i$ [4].

Since the potential of this technique is very great, and its use is becoming more and more widespread, the validity of eq. (2) in determining crystallite core size distributions needs to be assessed. For systems with broad

ordering size distributions, eq. (2) can have a vary significant influence *f(L)* essentially depends on $\Delta\nu_i^3$. We report here the results of a set of experiments designed to evaluate the quantitative aspects of this method in determining the distribution of ordered sequence lengths, to which distribution is directly related.

III. Calculations

The calculations were carried out with the Gaussian 94 program package. The possibilities of this package had limited the level of the calculations. Taking into account the atoms under the higher level "ab initio" methods only the Hartree-Fock method with LANL2DZ basis set (Los Alamos ECP plus DZ) was applicable to our task [11].

IV. Result and discussion

The structural investigation show, that region of well-ordered atoms accommodating in AS lye on greater domains, than the dimension of one structural units (s. u.). This brought the appearance of the conceptions of middle order in glassess [1-3]. On first stages of optical structural researches, in continuous Random Network (CRN) model radius of structural correlation, identified with clusters dimensions (dimensions of medium-range order), may be calculated from LF Raman measuring of spectrums [12].

The LF Raman spectrums of glass materials are characterized by the maximum (Boson peak), on the frequency position of which (ω_B) the dimensions of structural correlation (clusters dimensions) can be calculated. In mechanical theory of Phillips-Thorpe LF intensity of vibrations in glassess depends on the average coordination number z [13].

The resulted optimized geometries of the clusters have the following symmetries: C_{2v} for As_2S_3, C_s for As_2S_5 and As_6S_9, C_{3v} for As_4S_6 (fig.1). The geometry optimizations were followed by frequency calculations using the same basis set [14]. The maximum sizes of chain-lengths is: L=8.9 Å for As_2S_3, L=9.5 Å for As_2S_5, L=6.7 Å for As_4S_6, L=18.4 Å for As_6S_9 clusters.

The results of the low frequency calculations are presented (show) in fig. 2 together with the experimental LF Raman spectrums of different composition of As_xS_{100-x} system (See fig 2).

On the basis of the quantum-chemically calculated vibrational amplitudes of the As_2S_3 cluster one can give an approximate assignment of the vibrational modes. This molecule has nine vibrational modes, the irreducible representation contains seven in-plane ($4A_1+3B_2$) and two out-of-plane ones (A_2+B_1). The frequency of 62 cm^{-1} (A_1), can be considered as in-plane deformational mode. The last two frequencies, 41 (B_1) and 35 cm^{-1} (A_2) represent the symmetric and antisymmetric torsion modes of the S-As-S-As groups.

In cluster enriched by sulphur (As_2S_5) with C_s symmetry, LF oscillations have frequencies 3,5 and 11,3 cm^{-1}. For branch cluster As_4S_6 with symmetry (C_{3v}), LF vibrations are located at to 17,8 and 25,7 cm^{-1}. For branch cluster As_6S_9 with four final sulphur (As_6S_9) atoms with C_s symmetry six vibrations LF are found in region from 9 to 22 cm^{-1}. The LF torsion vibration are located in region from 17,8 to 25,7 cm^{-1}.

According to theoretical calculations the observed intensity of low-frequency Raman scattering $I_{obs}(\Delta\nu)$ in LF spectrum region Is determined by an equation:

$$I_{obs}(\Delta\nu)=C(\Delta\nu)\, g(\Delta\nu)\, [n(\Delta\nu)+1]/\Delta\nu \quad , \quad (3)$$

here $C(\Delta\nu)$ is the light-vibration coupling coefficient; $g(\Delta\nu)$ is the vibrational density of states (VDOS), $n(\Delta\nu)$ is the Bose factor.

Conventional to esteem reduced spectra:

$$I_{red}(\Delta\nu)=\Delta\nu I_{obs}(\Delta\nu)/[n(\Delta\nu)+1]=C(\Delta\nu)g(\Delta\nu), \quad (4)$$

The reduced Raman spectrum $I_{red}(\Delta\nu)$ for As_2S_3 and $As_{22}S_{78}$ glasses show in fig.2. (curve 2, 4).

Being grounded on inelastic neutron scattering and spectroscopic studies in [15] was calculated that in region $20 < \Delta\nu < 60$ cm^{-1}, $C(\Delta\nu)$ is proportional $\Delta\nu$ [$C(\Delta\nu)\approx\Delta\nu$]. Approximately it is possible to consider, that

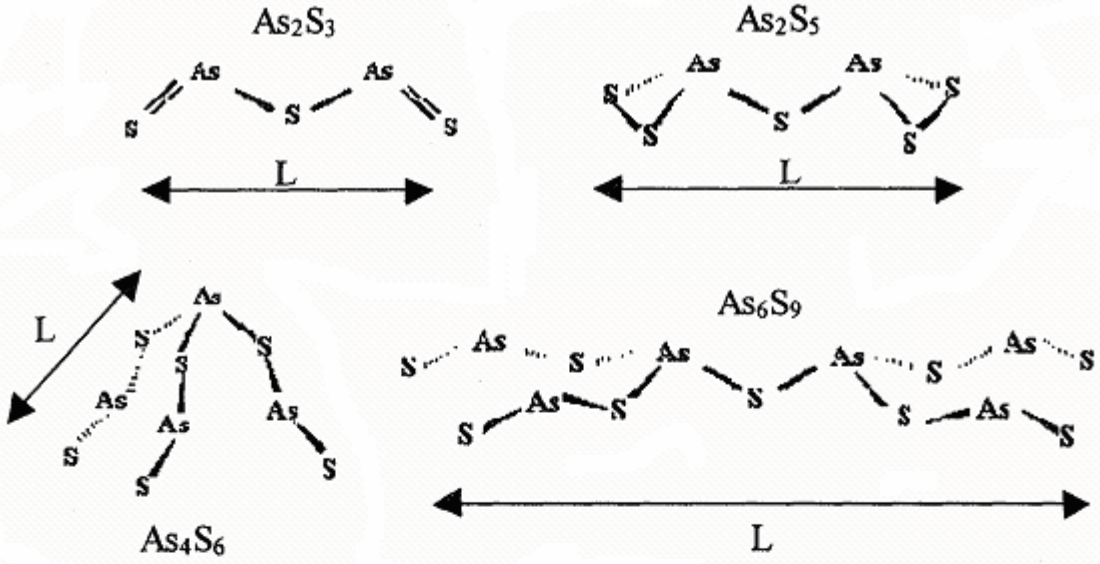

Fig.1. Optimal geometries structure for the calculated arsenic sulfide clusters As_nS_m and line sizes of chain sequences (L) in chain approximation.

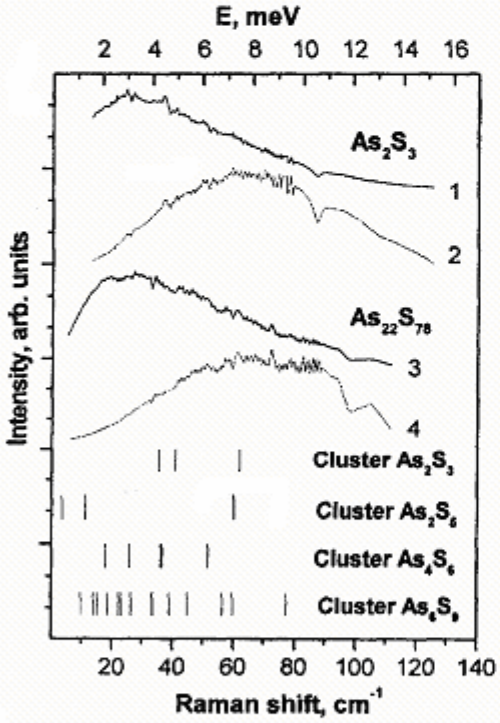

Fig.2. Low-frequency Raman (LFR) spectrums of As_2S_3 and $As_{22}S_{78}$ glasses exciting by 632,8 nm. laser illumination (1, 2 - observed spectrum (I_{obs}); 2, 4 – reduced spectrum (I_{red})) and "ab initio" calculations for different As_nS_m clusters.

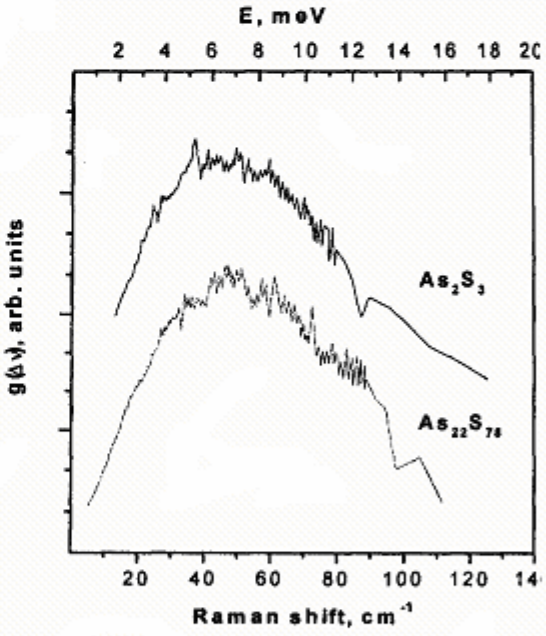

Fig.3. Vibrational density of states of As_2S_3 and $As_{22}S_{78}$ glasses in aproximation $C(\Delta\nu) \sim \Delta\nu$.

$C(\Delta\nu) \sim \Delta\nu$. Including this relation fair and in our case the equation (4) can be written as:

$$I^{*}_{red}(\Delta\nu) \approx I_{obs}(\Delta\nu)/[n(\Delta\nu)+1] = g(\Delta\nu). \quad (5)$$

Therefore in fig.3 we adduce relation $I^{*}_{red}(\Delta\nu)$, which indicate VDOS $g(\Delta\nu)$ for aproximation $C(\Delta\nu) \sim \Delta\nu$. In the results which are shown in a fig. 3, it is clear that the maximum of a VDOS lays near $\Delta\nu = 49$ cm^{-1} (E = 6,076 meV) for As_2S_3 (z=2.4) and $\Delta\nu = 46$ cm^{-1} (E=5,704 meV) for $As_{22}S_{78}$ (z=2.22) glasses. Correlating the VDOS by neutron inelastic scattering studies of glasses Ge-As-Se systems, described in [16] with our data as can see that maximum $g(\Delta\nu)$ is biased in LF region.

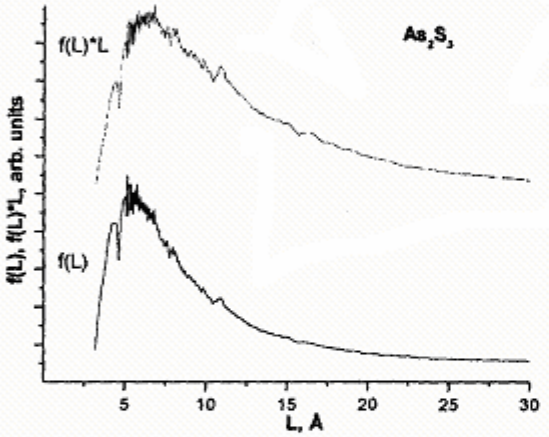

Fig.4. Cluster lengths distribution *f(L)* and weight distribution of cluster lengths *f(L)*L* for As_2S_3 glass calculated from observed Raman spectrum of fig.2.

For calculations as density of the clusters and Young's modulus we have used mean values for a glass, that could call definite discrepancies in lengths distribution *f(L)*. For a glass $As_{22}S_{78}$ we do not present lengths distribution *f(L)* because this glasses are present not only in chain clusters. Therefore the usage of chain approximating is rather contradictory. Besides there are difficulties with gravity determination and Young's modulus of clusters. The result of cluster lengths As_2S_3 glass, calculated from observed Raman spectrum is shown in fig.3. The cluster weight lengths for As_2S_3 glass may be changed from 6 to 11 Å by the weight distribution lengths *f(L)*L*.

V. Conclusions

Calculated Low-frequencies only torsion type of the large clusters are located in the same spectral region as Boson peak of amorphous semiconductors As-S system. They can made several contributions to the LF spectrum. In the intensity of the Boson peak besides the long-wavelength acoustical phonons torsional vibrations are present also. The average sizes of such cluster are changed from 6 to 11 Å.

VI. Acknowledgements

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НЧ КР СПЕКТРИ СТЕКОЛ As_xS_{1-x}, КОЛИВАЛЬНІ СПЕКТРИ КЛАСТЕРІВ As_nS_m, РОЗРАХОВАНИХ МЕТОДОМ "AB INITIO", ТА РОЗПОДІЛ КЛАСТЕРІВ ПО ДОВЖИНАМ

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Приведені результати порівняння спектрального положення НЧ смуг в стеклах системи As-S з теоретичними розрахунками коливального спектру різних кластерів (As_2S_3, As_2S_5, As_4S_6, As_6S_9) в НЧ області (5-100 cm^{-1}). Для скла As_2S_3 розраховано розподіл кластерів за довжинами в ланцюжковому наближенні.