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Solid State Communications 129 (2004) 655–659

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# Boson peak of $\text{As}_x\text{S}_{1-x}$ glasses and theoretical calculations of low frequencies clusters vibrations

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Received 30 October 2003; received in revised form 6 November 2003; accepted 18 November 2003 by S.G. Louie

## Abstract

The results of comparison of spectral position of the LF bands of  $\text{g-As}_2\text{S}_3$  and  $\text{g-As}_{22}\text{S}_{78}$  with theoretical calculations of vibrational spectra of different clusters ( $\text{As}_2\text{S}_4$ ,  $\text{As}_2\text{S}_5$ ,  $\text{As}_2\text{S}_6$ ,  $\text{AsS}_3\text{-As}_3$ ) in the LF region ( $10\text{--}85\text{ cm}^{-1}$ ) are given. The torsion type vibrations of the small chain-like clusters are located in the same spectral region as Boson peak of  $\text{As-S}$  glasses system. They can make several contributions to the LF spectrum. The cluster lengths by weight distribution functions  $f(L)*L$  are from 5.5 to 10.1 Å and from 4.5 to 7.5 Å for  $\text{g-As}_2\text{S}_3$  and  $\text{g-As}_{22}\text{S}_{78}$ , respectively. The lognormal fittings of the  $f(L)*L$  functions give the most probably values about the 7.6 Å (for  $\text{g-As}_2\text{S}_3$ ) and 6.2 Å (for  $\text{g-As}_{22}\text{S}_{78}$ ).

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PACS: 61.43. – j; 78.30. – j

Keywords: A. Chalcogenide glasses; E. Raman spectra; D. Boson peak; D. Size distribution; C. Ab initio calculation

## 1. I. Introduction

Non-crystalline materials, such as non-oxide glasses (especially chalcogenides), are important both for practical use and fundamental structural investigations [1]. A peculiar characteristic of disordered solids, not present in their crystalline counterpart [2], is an excess of low frequency states with respect to the predictions of the Debye theory. Inelastic neutron scattering studies on the density of states,  $g(\omega)$ , reveal a broad peak (so called Boson peak) in the quantity  $g(\omega)/\omega^2$  [3,4] at energies 2–10 meV, there Debye theory would predict a constant. The Boson peak (BP) is a fundamental feature of all glasses.

The nature of this excess of states is still subject for discussion and there are two different prevailing hypotheses [5]. In the first one, the excess of states is explained by the localization of the high-energy vibrational modes induced by the static disorder in the glass. In the second case, collective propagating modes are thought to persist at high frequency, and the BP reflects their density of states. In the

first view the BP energy corresponds to the energy of the high Q excitations, while in the second one the excitations are expected to propagate at energies above the BP energy.

The broad Boson peak feature is also observed in Raman scattering spectra of glassy semiconductors (GS) [6]. In their low frequency Raman spectra, all glasses show a broad feature around  $10\text{--}50\text{ cm}^{-1}$ . This Boson peak is identified with the existence of intermediate range order in the glass [7–9].

The idea of cluster arrangement of atoms or atomic bonds can be very helpful in understanding the physics of amorphous system. A low-frequency Raman measurement of GS is analyzed in order to find evidence for any possible cluster arrangement of GS. 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 size clusters and light scattering experiment of amorphous system [7–9]. This work has two aims: (1) the comparison of very low frequencies vibration of different  $\text{As}_n\text{S}_m$  clusters, studied by ab initio, with a position of the LF maximum (Boson peak) of  $\text{g-As}_2\text{S}_3$ ,  $\text{g-As}_{22}\text{S}_{78}$ , (2) calculation of a distribution function of the cluster lengths in chain-like model.

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## 2. Experiments and data analysis

Arsenic sulfide glasses were prepared by melting of elemental arsenic and sulfur in evacuated and sealed quartz ampoules, placed in a rocking furnace at 600 °C, for 24 h. These glasses were then cooled in air with cooling rate 1 K/s.

Raman spectra were measured in the right angle geometry, due to the big thickness of the samples. The DFS-24 spectrometer with a spectral slit width  $1 \text{ cm}^{-1}$  was used for measurements. Excitation laser beam 632.8 nm was used.

The sizes distribution of chain clusters may be calculated in chain-like approximation by ratio [10]:

$$L = \frac{m}{2c\Delta\nu_1} \left( \frac{E_c}{\rho} \right)^{1/2}, \quad (1)$$

here  $m$  is the mode order,  $c$  is the speed of light,  $\Delta\nu_1$  is the frequency shift in LF Raman spectra,  $E_c$  is the Young's modulus,  $\rho$  is the density of glass.

Broad size distributions are quite common and under these circumstances ratio (1) cannot be applied directly and some authors [11,12] obtained the relation

$$f(L_i) \propto \left[ 1 - \exp\left(-\frac{hc\Delta\nu_1}{kt}\right) \right] (\Delta\nu_1)^2 I_{\nu_i} \quad (2)$$

Here  $I_{\nu_i}$  is the observed scattering intensity at the frequency shift  $\Delta\nu_1$ . The factor  $[1 - \exp(-hc\Delta\nu_1/(kt))]$  is an intensity correction for the Boltzmann population of vibrational energy levels. The weighting factor  $(\Delta\nu_1)^2$  occurs in the equation because of the distribution function  $f(L_i)$  is defined for equal increments in  $L$ , while the spectrum is determined for increments in  $\Delta\nu_1$  [10].

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 very significant influence because  $f(L)$  essentially depends on  $(\Delta\nu_1)^3$ . We report here the results of a set of experiments designed to evaluate the quantitative aspects of this method in determining the distribution of chain-like cluster lengths, to which distribution is directly related.

## 3. Calculations

All the calculations were performed with the help of ab initio method using quantum-chemical program package GAMESS (US) [13]. The calculations described here are based on the restricted Hartree–Fock theory. The 6-31G\* basis set [14] with polarization d-functions for As and S atoms was used. To study LF Raman active modes of As–S glasses we use finite clusters of atoms containing structural units expected to be important in the glasses. The size of clusters is near line lengths by cluster size distribution

function from experimental LF Raman spectra. Dangling bonds on the cluster surfaces are terminated by H atoms, for better model of chemical environment of the glasses.

Atomic relaxation was taken into account by means of minimization of the total energy of the clusters. The clusters geometries are optimized using conjugate-gradient algorithm. Besides, using ab initio method we performed reference calculations optimizing the total energy of the clusters with respect to positions of all the atoms of the clusters.

The low frequencies vibrational (torsional) Raman active modes and eigenvectors are computed using standard techniques. To eliminate influence of the saturating hydrogen atoms on the vibrations localized in the defect, the masses of these atoms are assigned a very small value ( $10^{-4}$  a.u.) and so corresponding vibrations are completely suppressed. We also change to zero dipole derivative and alpha polarizability tensors elements by hydrogens atoms and then recalculate Raman modes using these modify tensors. So, the resulted modes do not contain practically any influence of hydrogen atoms.

## 4. Result and discussion

The structural investigation show, that region of well-ordered atoms accommodating in GS lie on greater domains, than the dimension of one structural units (s.u.). This brought the appearance of the conceptions of middle range order in glasses [7–9]. 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 [15].

The LF Raman spectrums of glass materials are

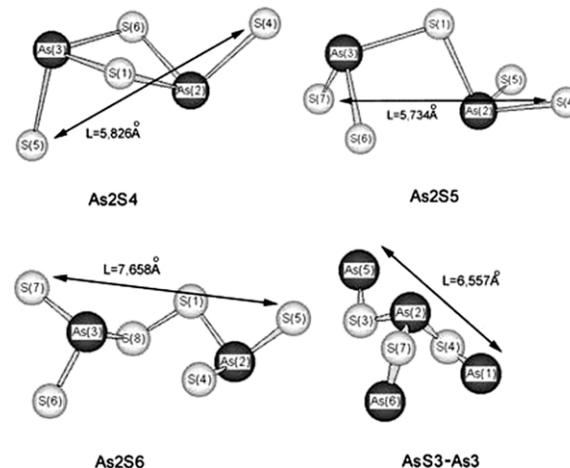


Fig. 1. Optimal geometries structure for the calculated arsenic sulfide clusters  $As_nS_m$  and maximum line sizes of clusters ( $L$ ) in line approximation.

Table 1  
Low frequencies Raman active modes of  $As_nS_m$  chain-like clusters calculated by ab initio and their approximate assignments

| Cluster      | LF modes, ( $cm^{-1}$ ) | Raman activities ( $\text{\AA}^4/\text{a.m.u.}$ ) | Approximate assignments   |
|--------------|-------------------------|---|---|
| $As_2S_4$    | 46.65                   | 0.528   | Torsional vibrations of $AsS_3$ pyramids around $S_1-S_6$ line.   |
| $As_2S_5$    | 24.13                   | 1.607   | Torsional vibrations of $AsS_3$ pyramids around $S_1$ atom.   |
|              | 45.89                   | 1.736   | Torsional vibrations of $AsS_3$ pyramids around $S_1$ atom.   |
|              | 76.90                   | 1.316   | Deformation vibration of $As_3-S_1-As_2$ angle  |
| $As_2S_6$    | 17.67                   | 0.906   | Torsional vibrations of $AsS_3$ pyramids around $S_8$ atom.   |
|              | 37.23                   | 2.22  | Torsional vibrations of $AsS_3$ pyramids around $S_1$ atom.   |
|              | 54.40                   | 0.945   | Torsional vibrations of $AsS_3$ pyramids around $S_1-S_8$ line.   |
| $AsS_3-As_3$ | 17.21                   | 1.123   | Torsional vibration of $S_3As_5$ pyramid.   |
|              | 22.97                   | 2.303   | Torsional vibration of $S_4As_1$ pyramid.   |
|              | 47.17                   | 0.916   | Torsional vibration of $S_7As_6$ pyramid.   |
|              | 74.88                   | 2.461   | Torsional vibrations of $As_2S_2$ pyramids ( $As_2S_{3,4}$ ) and deformation vibrations of $As_2-S_3-As_5, As_1-S_4-As_2$ angles. |

characterized by the maximum (BP), on the frequency position of which ( $\omega_B$ ) the dimensions of structural correlation (clusters dimensions) can be calculated. In mechanical theory of Phillips-Thorpe LF intensity of vibrations in glasses depends on the average coordination number  $z$  [16].

The result of optimized geometries of the clusters is shown in Fig. 1. The geometry optimizations were followed by frequency calculations using the same basis set. The maximum sizes of clusters are:  $L = 5.826 \text{ \AA}$  for  $As_2S_4$ ,  $L = 5.734 \text{ \AA}$  for  $As_2S_5$ ,  $L = 7.658 \text{ \AA}$  for  $As_2S_6$ ,  $L = 6.557 \text{ \AA}$  for  $AsS_3-As_3$  clusters (Fig. 1).

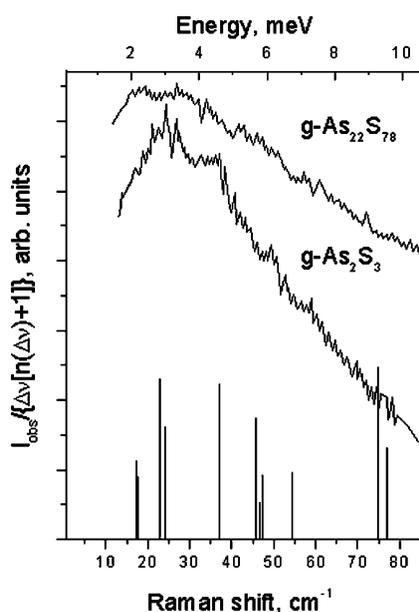


Fig. 2. Reduced LF Raman spectra of  $g-As_2S_3$  and  $g-As_{22}S_{78}$  glasses exciting by 632.8 nm. laser illumination and LF Raman modes calculated by ab initio method for different  $As_nS_m$  clusters.

The results of the low frequency calculations are shown in Fig. 2 together with the reduced LF Raman spectra of different composition of  $As_xS_{100-x}$  system (see Fig. 2). On the basis of the quantum-chemically calculated vibrational amplitudes of the  $As_nS_m$  clusters it can be given an approximate assignment of the vibrational modes. Every cluster have  $3N - 6$  normal modes (where  $N$  is a number of atoms), but we analyse only very low frequency vibrations (region of BP position in  $As_xS_{1-x}$  glasses). The calculated LF Raman active modes and their assignments for each model clusters are shown in Table 1.

In our previous researches [17] LF modes on  $As_2S_3$ ,  $As_2S_5$  (with S–S bonds on the end) and more larger  $As_4S_6$ ,  $As_6S_9$  clusters using Gaussian software were also calculated (see [17] for detail). The maximum sizes of chain-lengths are:  $L = 6.7 \text{ \AA}$  for  $As_2S_3$ ,  $L = 7.3 \text{ \AA}$  for  $As_2S_5$ ,  $L = 4.2 \text{ \AA}$  for  $As_4S_6$ ,  $L = 14 \text{ \AA}$  for  $As_6S_9$  clusters.

On the basis of the quantum-chemically calculation the  $As_2S_3$  cluster has nine vibrational modes. There are only two lowest 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 vibrations 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  $C_3$  symmetry six LF vibrations are found in region from 9.6 to 22.9  $cm^{-1}$ .

According to theoretical calculations the observed intensity of low-frequency Raman scattering  $I_{obs}(\Delta\nu)$  in low-frequency spectrum region is determined by an Eq. [18]:

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

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:

$$I_{red}(\Delta\nu) = I_{obs}(\Delta\nu)/\{\Delta\nu[n(\Delta\nu) + 1]\} = C(\Delta\nu)g(\Delta\nu)/(\Delta\nu)^2 \tag{4}$$

Being grounded on inelastic neutron scattering and spectroscopic studies in [19] it was calculated that in region  $20 < \Delta\nu < 60 \text{ cm}^{-1}$ ,  $C(\Delta\nu)$  is proportional to  $\Delta\nu [C(\Delta\nu) \approx \Delta\nu]$ . Approximately it is possible to consider, that  $C(\Delta\nu) \sim \Delta\nu$ . Taking into account this relation fair in our case the Eq. (4) can be written as:

$$g(\Delta\nu) = I_{red}(\Delta\nu)(\Delta\nu)^2/C(\Delta\nu) \approx I_{red}(\Delta\nu)\Delta\nu = I_{obs}(\Delta\nu)/[n(\Delta\nu) + 1]. \tag{5}$$

Therefore in Fig. 3 we adduce relation (5), which indicate VDOS  $g(\Delta\nu)$  for approximation  $C(\Delta\nu) \sim \Delta\nu$ . In the results which are shown in a Fig. 3, it is clear that the maximum of a VDOS is near  $\Delta\nu = 51 \text{ cm}^{-1}$  ( $E = 6.3 \text{ meV}$ ) for  $g\text{-As}_2\text{S}_3$  ( $\tau = 2.4$ ) and  $\Delta\nu = 45.5 \text{ cm}^{-1}$  ( $E = 5.6 \text{ meV}$ ) for  $g\text{-As}_{22}\text{S}_{78}$  ( $\tau = 2.22$ ). Correlating the VDOS by neutron inelastic scattering studies of Ge–As–Se glass system, described in [20] with our data as can be seen the maximum  $g(\Delta\nu)$  is located in LF region.

The results of model chain-like clusters lengths for  $g\text{-As}_2\text{S}_3$  and  $g\text{-As}_{22}\text{S}_{78}$ , calculated from observed Raman spectrums are shown in Fig. 4. The chain-like clusters lengths for  $g\text{-As}_2\text{S}_3$  and  $g\text{-As}_{22}\text{S}_{78}$  changed from 5.5 to 10.1 Å and from 4.5 to 7.5 Å respectively by the weight distribution (Fig. 4) lengths functions  $f(L)*L$ . The lognormal fittings of the weight distribution lengths functions

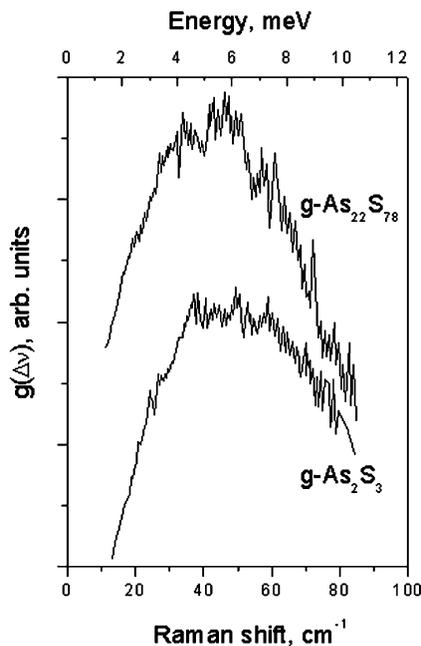


Fig. 3. Vibrational density of states of  $g\text{-As}_2\text{S}_3$  and  $g\text{-As}_{22}\text{S}_{78}$  glasses in approximation  $C(\Delta\nu) \sim \Delta\nu$ .

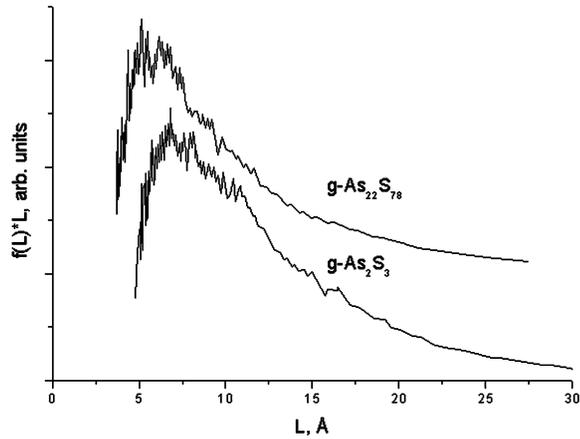


Fig. 4. Weight distributions of ordered chain-like cluster lengths for  $g\text{-As}_2\text{S}_3$  and  $g\text{-As}_{22}\text{S}_{78}$  calculated from observed Raman spectrum.

$f(L)*L$  give the most probably values about the 7.6 Å (for  $g\text{-As}_2\text{S}_3$ ) and 6.2 Å (for  $g\text{-As}_{22}\text{S}_{78}$ ). For calculations both density and Young’s modulus we have used mean values for glasses, that could cause definite discrepancies in lengths distribution.

### 5. Conclusions

Only torsion type of calculated low-frequencies of the model clusters are located in the same spectral region as Boson peak of amorphous semiconductors As–S system. They can make several contributions to the LF spectrum. The intensity of the Boson peak is influenced both the long-wavelength acoustical phonons and low frequency modes (torsional vibrations) localized in small chain-like clusters. The cluster lengths by weight distribution functions  $f(L)*L$  are from 5.5 to 10.1 Å and from 4.5 to 7.5 Å for  $g\text{-As}_2\text{S}_3$  and  $g\text{-As}_{22}\text{S}_{78}$ , respectively.

### Acknowledgements

The authors are grateful to N. Mateleshko for many valuable discussions. Her contribution to this work is sincerely appreciated. This work was supported by Ukrainian Ministry of Science and Technology. Grant No. M/467-2003 and Grant No. 29/48-2001.

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