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An EXAFS-study of reversible photostructural changes in As_2Se_3 glass

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Reversible photostructural changes in a binary As_2Se_3 glass have been studied by high-precission in-situ EXAFS. We demonstrate that the coordination number of selenium species increases reversibly in the photoexcited state while the coordination number for arsenic species remains unchanged which is attributed to creation of dynamical Se–Se interlayer bonds. Photoexcitation increases disorder around both selenium and arsenic species. Following photoexcitation, bond breaking takes place restoring initial coordination number of both constituents and creating "wrong" As–As and Se–Se bonds.

Reversible photostructural changes in chalcogenide glasses have been known since early 70*s* when reversible photoinduced changes in optical absorption of As_2S_3 and As_2Se_3 were reported [1]. X-ray diffraction studies have established that these changes were caused by reversible changes in the structure [2]. Although phenomenology of the process is now well understood within the configuration-coordinate model [3–5], their microscopic nature still remains a challenge. Raman studies performed on As_2S_3 have detected a reversible photo-induced increase in the concentration of so-called "wrong" As–As bonds [6] which was later confirmed by EXAFS-studies [7] for the same material. In addition, EXAFS have detected a change in the second coordination sphere of arsenic species. These data indicated importance of arsenic in the photostructural changes. However, it should be remembered that the photostructural change cannot be observed in pure amorphous arsenic [8] while it is observed in elemental amorphous chalcogens, both selenium and sulphur [9]. Thus, it seems more natural to seek the origin of the photostructural change in behaviour of chalcogen species. Our recent high-precision in situ EXAFS-studies have revealed that the coordination number of amorphous selenium (*a*-Se) increased reversibly in the photoexcited state [10] and the microscopic description for the photostructural change was given as follows. Under photoexcitation, one of the lone-pair (LP) electrons which form the top of the valence band, is excited into the conduction band while the other one is left unpaired in the former LP-orbital. Such photoexcited atoms are stabilised by formation of additional interchain bonds making about 10% of Se atoms 3-fold coordinated. Following the photoexcitation, bond-breaking takes place leading to creation of valence-alternation defects and bond switching, as demonstrated in Fig. 1.

In this paper, we report the data for the photostructural change in a model binary glass As_2Se_3 which demonstrate that the model suggested earlier is quite general and is also correct in case of binary chalcogenides.

1. Experimental details and data analysis procedure

The samples were prepared by thermal evaporation of bulk Ad_2Se_3 glass onto a Corning-glass substrate in a vacuum of 10^{-6} Torr and had a thickness of ~ 1000 Å. This composition was chosen since both Se and As K-edges, being very close to each other, can be measured simultaneously. The measurements were performed at BL13B station at the Photon Factory [11] using a 27-pole wiggler magnet inserted in a 2.5 GeV storage ring. We have chosen a fluorescence mode because of the fact that the samples with thicknesses smaller than the band-gap light penetration depth should be probed. Either arrays of 19-element high-purity Ge solid-state detectors or 9 NaI(Tl) scintillation counters were used to detect the fluorescence. EXAFS-spectra with good signal–to–noise ratio were obtained for thin films with a thousand Angstrom thickness.

Combination of high brilliance photon source and a densely packed detector array allowed us to improve the efficience of fluorescence excitation and detection by two orders of magnitude. A directly water-cooled Si(111) double-crystal monochromator [12] provided a stable and intense X-ray beam with an energy resolution of ~ 2 eV at 9 keV. High precision was achieved by in-situ monitoring of the fluorescence monitoring the same region of uniform (evaporated film) sample at low temperature maintained within ±0.1 K.

We have estimated possible uncertainties in the obtained values caused by the non-systematic noise, i.e., photon counting statistics and electronic noise. Although it is difficult to estimate the systematic noise, we believe that the dominant source of error in our in-situ experiments is beam instability since the effect of inhomogeneity in sample thickness is not present. We followed the recommended procedure [13] and measured several independent scans consecutively for a film of crystalline selenium which does not undergo structural transformations. The scatter in the data never exceeded ±0.5%, which clearly demonstrates that in-situ measurements under these conditions allowed us to achieve the

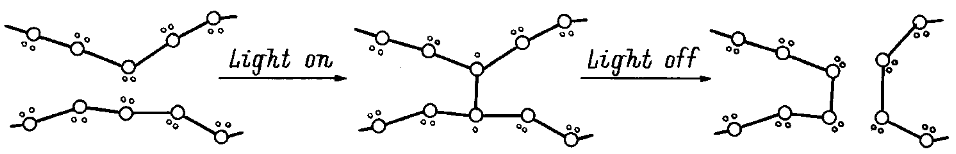

Fig. 1. Schematic presentation of the photo-induced structural change in amorphous selenium after [10].

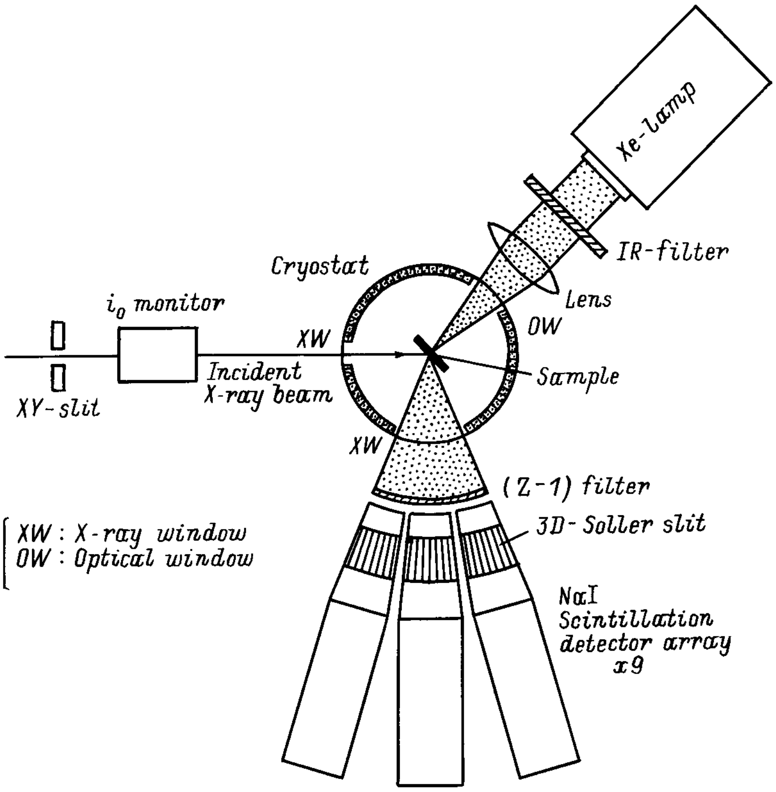

Fig. 2. Experimental setup.

accuracy in a relative change in coordination number and mean-square relative displacement (MSRD) within ±1% (compared to ±20% for conventional ex-situ EXAFS).

The sample was mounted on an aluminium holder in an evacuated cryostat equipped with windows (KAPTON) for incident and fluorescent X-ray beams as well as an optical window (MYLAR) for in-situ light irradiation. A 500 W Xenon lamp with an IR-cutoff filter was used as an excitation source. The light was focused onto a 15 mm diameter spot for which the light intensity on the surface of the sample varied from 50 to 250 mW/cm^2. In order to avoid heating of the sample during the irradiation, a closed-cycle He refrigerator with a cooling power of $\sim$ 9 W at 20 K was used even though measurements were done at room temperature. A schematic diagram of the experimental setup is illustrated by Fig. 2.

Since we were only interested in a photo-induced relative change in the coordination and disorder we have applied the ratio method for the data analysis. The essence of this method is given below.

Within a single-scattering approximation, the EXAFS is given by the following expression

$$\chi(k) = -\sum(N_j/R_j^2)(f_j|k|/k)\exp(-2R_j/\lambda_c)$$
$$\times \exp(-2\sigma_j 2k^2)\sin\Big(2kR_j + 2\delta(k) + \eta_j(k)\Big), \quad (1)$$

where a sum over all shells of atoms, j, is taken, each containing N_j atoms at a distance R_j from the absorbing atom. The magnitude of EXAFS is proportional to N_j, inversely proportional to R_j^2 and proportional to the back-scattering amplitude $[f_j(k)|$ from the atoms in the j th shell. The amplitude is attenuated because of the finite mean free path λ_c and by mean-square relative displacement (MSRD) involving both static and thermal disorder. Finally, the amplitude is sinusoidally modulated by a function involving a phase shift of the electrons, δ and η.

If two different measurements are taken in various condition, then the ratio of the two spectra, in the assumption of unchanged bond length, is given as

$$\chi_2(k)/\chi_1(k) = 2(\sigma_1^2 - \sigma_2^2)k^2 + \ln(N_2/N_1). \quad (2)$$

One can see that the slope of the line gives a change in the disorder parameter while the intersection with y-axis gives a change in the coordination number. An important advantage of this technique is that it allows one to separate the contributions from the coordination number and disorder in the change in the spectra. As can be seen from Eq. (1), these parameters are strongly correlated are often difficult to be separated. The use of the ratio method is justified by the unchanged bond length in the photoexcitation cycle observed for elemental selenium [10].

2. Results

Fig. 3 shows fluorescence yield normalised by the incident beam intensity for Se K-edge (Fig. 3,a) and As K-edge (Fig. 3,b). In Fig. 4 Se and As K-EXAFS oscillations are shown as a function of photoelectron wavenumber k for Se (Fig. 4,a) and As (Fig. 4,b) K-edges after subtraction of smooth backgrounds due to the atomic absorption from the fluorescence yield spectra. The background function given as a combination of the third and fourth order polynomials, with tabulated coefficients [14] (Victoreen Function) smoothly interpolates EXAFS-oscillations. The cubic spline function was normalized to the edge jump and subtracted from the fluorescence yield spectrum.

The results for the ratio method are summarized in Fig. 5 where the ratios of EXAFS spectra for Se K-edge (Fig. 5,a) and As K-edge (Fig. 5,b) are shown. The EXAFS-spectra in the photoexcited state (top) and photodarkened, but no longer photoexcited (bottom) are divided by the spectrum for the annealed sample. One can see that in the photoexcited state the coordination and disorder around Se species increase accompanied by an increase in disorder for As species. The coordination number for As species remains unchanged. After switching off the light the coordination number for selenium acquires its original value and disorder around both selenium and arsenic species slightly decreases. The fitting of the experimental points for the photoexcited Se K-edge by a straight line given by Eq. (2) gives an increase in the coordination of 10 ± 5% in the photoexcited state. The observed behaviour for selenium in As_2Se_3 is identical to that in elemental amorphous selenium [10].

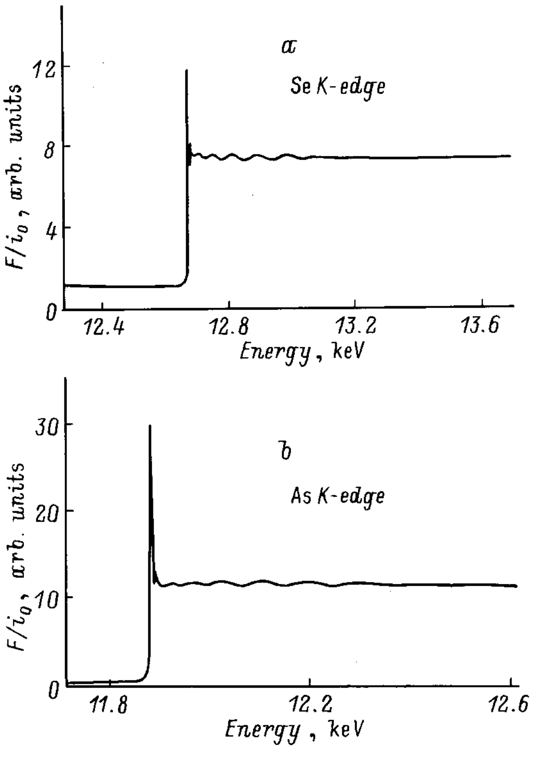

Fig. 3. Fluorescence yields for Se (a) and As (b) K-edges.

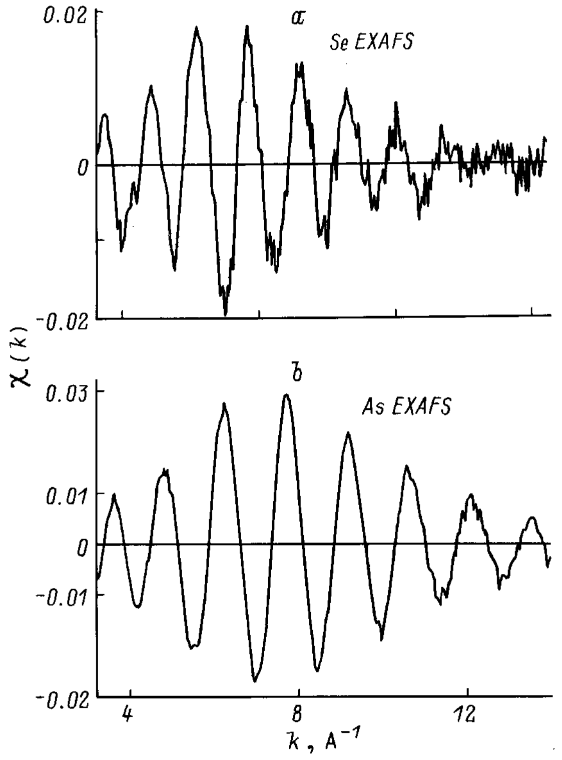

Fig. 4. Raw EXAFS-oscillations for Se (a) and As (b) K-edges as a function of wave number k.

3. Discussion

The observed results demonstrate that the model suggested for elemental selenium is quite general and is also applicable to compound chalcogenides. Similar picture can be presented for a local structure of As_2Se_3 as shown in Fig. 6 which presents a cross-sectional view of As–Se layers. Different from the case of elemental selenium, atoms with odd numbers represent chalcogen and atoms with even numbers stand for arsenic. In the photoexcited state, unpaired electrons of former LP-orbitals can form bonds between the layers resulting in an increase in the coordination number of selenium and

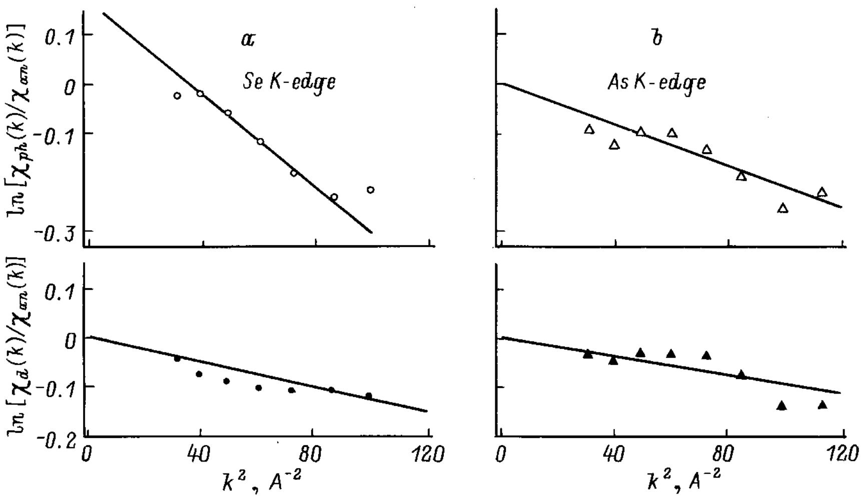

Fig. 5. Results of ratio method analysis of EXAFS-spectra for Se K-edge (a) and As K-edge (b). The ratio is taken for the photoexcited sample over annealed sample (top) and photodarkened, but no longer photoexcited sample, over annealed sample (bottom).

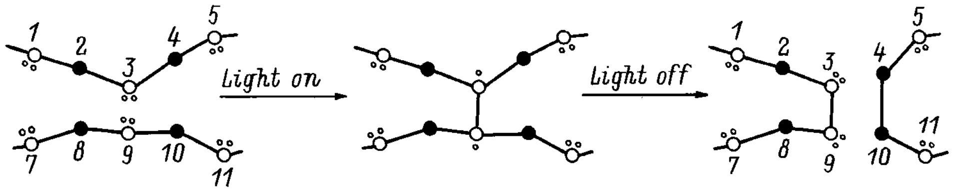

Fig. 6. Schematic presentation of the photostructural change in As_2Se_3 glass.

in disorder for both selenium and arsenic species. When subsequent bond breaking takes place the structure is converted to the one shown on the right-hand side of the figure. One can see that bond switching analogous to that shown in Fig. 1 for elemental selenium now leads to the formation of "wrong" As–As and Se–Se bonds with the same coordination number as in the case of the annealed film.

Formation of As–As wrong bonds was experimentally detected by EXAFS for As_2S_3 [7]. In our case we cannot distinguish between As–As, Se–Se and As–Se bonds because As and Se are nearest neighbours in the periodic tables and have very similar backscattering amplitude. However, we can probe the local structure of both As and Se. Previous experiment was done for As_2S_3. Rather different atomic numbers of the two glass components allowed to detect the formation of As–As bonds but measurements of S K-edge was impossible since this required a different X-ray source (soft X-rays). The two experiments are thus complementary and demonstrate that the observed mechanism probably also takes place in As_2S_3 glass.

Application of high-precision in-situ EXAFS for photostructural changes in a binary As_2Se_3 glass have demonstrated that the coordination of chalcogen species increases reversible in the photoexcited state while that of arsenic remains unchanged. Disorder increases for both selenium and arsenic species. After the photoexcitation initial coordination number is restored and the photo-induced disorder slightly decreases. The observed behaviour for selenium species is identical to that in elemental selenium which demonstrates that the basic mechanism underlying the photostructural changer in chalcogenide glasses is quite general and involves bond switching via the formation of dynamical bonds between photoexcited chalcogen atoms.

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