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SHORT – RANGE ORDER PARAMETERS IN AMORPHOUS YBaS₄X₇(X – S, SE, TE) FILMS

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Electron scattering intensity curves from amorphous YbAs₄X₇(X – S, Se, Te) films have been obtained by the transmission electron diffraction (TED) method with rotation sector before screen up. The energy of electrons was 100 keV. Amorphous samples were crystallized and the composition of the products were measured by TED. The atomic radial distribution function has been calculated by the Fourier synthesis of intensities in the TED of amorphous YbAs₄X₇(X – S, Se, Te) films. The interatomic average distances of As – S (Se, Te) and As – Yb²⁺ and partial coordination numbers have been estimated in these films. Based on these numbers, chemical orders in these films differ. This difference is due to differing topological order in the amorphous YbAs₄X₇(X – S, Se, Te) thin films.

The amorphous semiconductor materials, containing f – elements, represent a new class of amorphous materials. Thin films have begun to be studied recently [1-2]. These types of material have potential use as materials, containing magnet f – elements (rare earth elements-REE) [3]. There are data confirming the possibility of utilization of these materials in acousto-optics [4]. The systems Ln-As-X represent this class of materials, where Ln=REE. Such systems are mentioned in refs. [5-6].

At interaction of amorphous As₂X₃(X-S, Se, Te) films with polycrystalline Yb films the selective formation of YbAs₄X₇ is observed. Process of other phases formation is limited to dominant formation of this phase. The data about formation of amorphous films and their short – range order parameters are absent in literature.

Therefore, the purpose of the present work is determine the short – range order parameters in amorphous films of the YbAs₄X₇(X – S, Se, Te) compounds and to compare obtained data.

To obtain amorphous thin films of YbAs₄X₇(X – S, Se, Te) we applied a method of evaporation from a quasi reserve volume. As substrates we used air – cleaved NaCl (100) surfaces. The film thickness was calculated from the mass and density of the evaporating matter and was about 40 nm.

The composition of films was determined by the crystallization results of amorphous films in the formation of polycrystalline YbAs₄X₇(X – S, Se, Te) with lattice parameters similar to those in ref.[7].

We used the transmission electron diffraction (TED) method. The energy of electrons was 100 keV. The films were separated from the NaCl substrates by dissolving the salts in distilled water and the films were then placed on grids. After drying at room temperature, the samples were mounted on grids of EG, EMR – 102 or EG – 100 electronographs for examination. We used also the rotation sector before the screen of the electronographs to record the largest scattering angle.

Electron scattering curves were obtained with rotation sector up to S_{max}=10 Å⁻¹ for YbAs₄S₇, S_{max} =11,2 Å⁻¹ for YbAs₄Se₇, S_{max} =12 Å⁻¹ for YbAs₄Te₇.

The structure factor was normalized by the method of mean atom density [8].

For determination of the parameters of the short-range order, we used the atomic radial distribution function (ARDF) method [9,10].The structure in this method is described by the formula

$$4\pi r^2 \sum_i \sum_j c_i k_i k_j \rho_{ij}(r) = 4\pi r^2 \rho_0 (\sum_i c_i k_i)^2 + \frac{2r}{\pi} \alpha \int_0^{s_2} si(s) \sin sr ds, \quad (1)$$

where $\rho_{ij}(r)$ is the atom density of j-type atoms around an i-type atom, ρ_0 is the mean density of atoms, α is the normalization multiplier, $i(s)$ is the interference function, which is calculated directly from the corrected and normalized intensity, $s=4\pi\sin\theta/\lambda$, θ is the angle of scattering, and λ is the wavelength of electrons. In this work, the atoms are labeled: 1-atom of Yb, 2-atom of As, 3-atom of S (Se,Te). Coefficients c_i in eq. (1) are the

fractional concentration of element i . For YbAs_4S_7 $c_1=0,09$, $c_2=0,33$, $c_3=0,58$; for YbAs_4Se_7 $c_1=0,09$, $c_2=0,33$, $c_3=0,58$, for YbAs_4Te_7 $c_1=0,09$, $c_2=0,33$, $c_3=0,58$. The relative scattering ability for each element was calculated from the formula [8]

$$K_i = \left\langle f_i(s) / \sqrt{\sum_i c_i f_i^2(s)} \right\rangle \quad (2)$$

where $f_i(s)$ is the scattering factor of element i and $\langle \rangle$ is the average K_i .

After averaging K_i , we obtained $K_{\text{Yb}}=2.00$, $K_{\text{As}}=1.098$, $K_{\text{S}}=0.625$ for YbAs_4S_7 , $K_{\text{Yb}}=1.666$, $K_{\text{As}}=0.904$, $K_{\text{Se}}=0.912$ for YbAs_4Se_7 , $K_{\text{Yb}}=1.245$, $K_{\text{As}}=0.706$, $K_{\text{Te}}=1.094$ for YbAs_4Te_7 . The average atom densities were calculated by the formula [8].

$$\rho_0 = \rho N_A / \sum_i c_i A_i \quad (3)$$

where ρ is the density in g/cm^3 of either compound in the crystalline state, A_i is the atomic mass, $i=1,2,3$ in the chemical formula, and N_A is Avagadro's number. From the experimental intensity combined with eq. (1), we calculated the ARDF for amorphous YbAs_4X_7 ($X = \text{S}, \text{Se}, \text{Te}$) films in compliance with the procedure as reported earlier in refs.[9,10].

From the positions of the coordination maxima, we obtained the radii of the first and second coordination spheres. For determining the partial coordination numbers in the first coordination sphere, we calculated the areas under the maxima in the ARDF of amorphous YbAs_4X_7 ($X = \text{S}, \text{Se}, \text{Te}$) by the Simpson method. The partial coordination numbers were determined by the formula [8]

$$\sum_i \sum_j c_i k_i k_j n_{ij} = Q \quad (4)$$

where n_{ij} is the number of the atoms of j -type around one atom of i -type (partial coordinate number), Q_1 is the area under the first maximum on the ARDF (4.60 for the YbAs_4S_7 , 3.56 for YbAs_4Se_7 , 2.66 for YbAs_4Te_7) and c_i and k_i are as described above.

Electron diffraction patterns from amorphous and crystallized YbAs_4S_7 films are obtained. The pattern from crystallized YbAs_4S_7 films was identified on the base of parameters shown in ref. [7]. After obtained the normalization multiplier and constructing the interference function (fig. 1), the ARDF for amorphous YbAs_4S_7 was calculated. It is presented in fig. 2.

The radii of the first and second coordination spheres in amorphous YbAs_4S_7 are $2.36 \pm 0.01 \text{ \AA}$ and $3.64 \pm 0.01 \text{ \AA}$. All compounds $\text{Yb}_x\text{As}_y\text{S}_z$ are obtained by synthesis of ytterbium and As_2S_3 . Therefore we compared the distances between atoms in YbAs_4S_7 with the distanced between atoms in As_2S_3 . Increase of radii of coordination spheres in YbAs_4S_7 when compared with amorphous As_2S_3 ($r_1=2.25 \text{ \AA}$, $r_2=3.52 \text{ \AA}$) is attributed to the introduction of the Yb^{2+} ions in disordered networks of As_2S_3 . The sum of the covalent radii of arsenic and sulphur of the covalent radii of arsenic and sulphur ($r_{\text{as}}^{\text{cov}} + r_{\text{s}}^{\text{cov}} = 2.25(\text{A}^\circ)$) is approximately equal to the first coordination maximum $r_1 = 2.36 \text{ \AA}$, in the ARDF of YbAs_4S_7 .

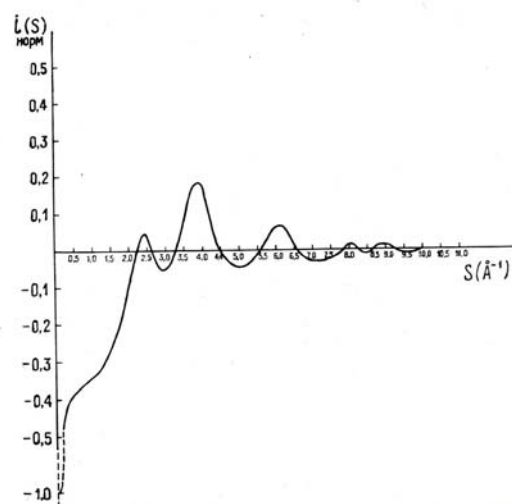


Fig.1 The normalized experimental $i(s)$ function for amorphous YbAs_4S_7 film.

Covalent and ion radii are taken from ref.(11). Besides, on the approximate equality mentioned above, we assume that the first coordination sphere of arsenic or sulphur is sulphur or arsenic, respectively. Some difference result in a decrease of atomic dense packing in the first coordination sphere of arsenic and sulphur atoms of amorphous YbAs_4S_7 and influence of Yb^{2+} ions on the $\text{As} - \text{S}$ bond. From the interpretation of the first coordination maximum we deduce that the bond between arsenic and sulphur is predominantly covalent in YbAs_4S_7 . The sum of the distance $\text{As} - \text{S}$ and radii of Yb^{2+} ion ($r_i + r_{\text{Yb}^{2+}} = 2.36 + 1.07 = 3.42\text{A}^\circ$) is close to the value of distance, r_2 corresponding to the second maximum on the ARDF of YbAs_4S_7 . It follows that the ions of Yb^{2+} are in the second coordination sphere. Some difference between the sum and r_2 is due to a decrease of the dense atom packing in the second coordination sphere of arsenic and sulphur in amorphous YbAs_4S_7 . [12].

The partial coordination numbers YbAs_4S_7 were determined: $n_{13} = 2$, $n_{23} = 3$, $n_{32} = 2$, $n_{31} = 4$ and $n_{11} = n_{12} = n_{22} = n_{21} = n_{33} = 0$. The coordination number of Yb^{2+} in YbAs_4S_7 is 2.

The partial coordination numbers and the distance between atoms in YbAs_4Se_7 and YbAs_4Te_7 were determined by the same method as for YbAs_4S_7 . We obtained for YbAs_4Se_7 : $n_{13}=3$, $n_{32}=3$, $n_{31}=1$, $n_{11}=n_{22}=n_{33}=n_{12}=n_{21}=0$ and for YbAs_4Te_7 : $n_{13}=0$, $n_{23}=1$, $n_{31}=2$, $n_{11}=n_{22}=n_{33}=n_{12}=n_{21}=0$. The radii of the first and second coordination spheres in amorphous YbAs_4Se_7 are $r_1=2,50 \text{ \AA}$ and $r_2=3,75 \text{ \AA}$; $r_1=2,56 \text{ \AA}$ and $r_2=3,82 \text{ \AA}$ in amorphous YbAs_4Te_7 .

The main interest in these materials is the environment of the rare earth atom because it determines the electric, optic and magnetic properties of these materials. We propose that the Yb^{2+} ions decrease the share of ionic bond between arsenic and khalcogen atoms as compared with As_2X_3 ($X = \text{S}, \text{Se}, \text{Te}$) and the distance between arsenic and khalcogen atoms is therefore larger as compared with their distance in As_2X_3 ($X = \text{S}, \text{Se}, \text{Te}$), although in As_2X_3 ($X = \text{S}, \text{Se}, \text{Te}$) the atoms of arsenic and sulphur are also the nearest neighbours.

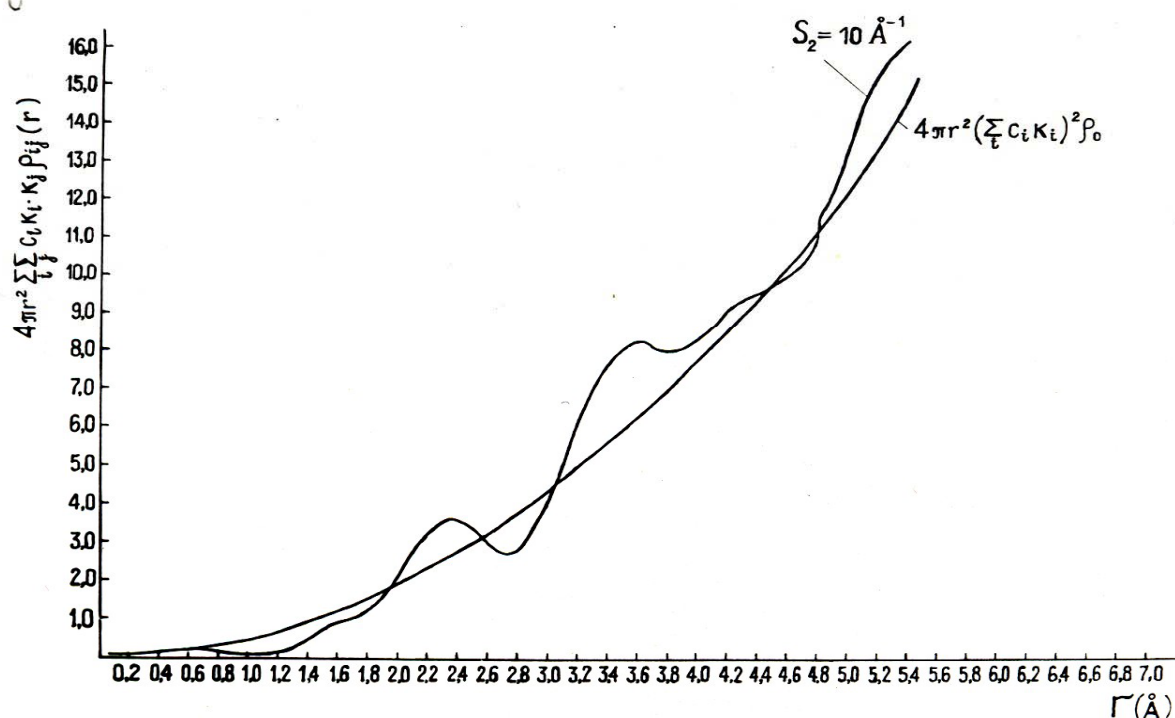


Fig. 2. The curve of radial distribution function of atoms for amorphous YbAs_4S_7 film.

Our data from ARDF show that the first coordination sphere of arsenic or khalcogen is khalcogen or arsenic, respectively. It is necessary to note that in the amorphous YbAs_4X_7 (X- S, Se, Te) we obtained the decrease of atomic dense packing in the first coordination sphere of arsenic and khalcogenid atoms relative to amorphous As_2X_3 (X- S, Se, Te). We assume that the Yb^{2+} ions influence the length of connection As - X (X- S, Se, Te) and its difference in these of the composition is due to a different amount of Yb^{2+} in these compositions.

In the present work we compared short range order in amorphous YbAs_4X_7 (X- S, Se, Te) thin films. It was shown that arsenic and khalcogenid atoms in amorphous YbAs_4X_7 (X- S, Se, Te) compounds are the nearest

neighbours and Yb^{2+} ions influence the As - X (X- S, Se, Te) connection. We concluded these compounds have great differences in an Yb^{2+} ions environment, i.e., different partial coordinate numbers (n_{12} and n_{13}) have been obtained for Yb^{2+} ions.

We determined that in the first coordination sphere of Yb^{2+} there are three atoms of arsenic YbAs_4Se_7 and YbAs_4Te_7 , but for YbAs_4S_7 in the same coordination sphere there are two atoms of sulphur. The coordination numbers of arsenic and in their first coordination sphere are different too. From these structural data we propose that electric, optic and magnetic properties of these materials must be different.

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