

X-RAY ABSORPTION SPECTRA OF CESIUM IONS IN SODIUM BOROSILICATE AND ALUMOPHOSPHATE GLASSES

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The x-ray absorption spectroscopy EXAFS (extended x-ray absorption fine structure) is used effectively for determination of the positions of heavy metal atoms and ions in the structure of crystalline materials and glasses [1]. In particular, this method was used to study the cesium structural state in some simple glasses [2-4]. The objective of the present study is to determine the structural parameters from EXAFS spectra of the cesium L_3 edge in sodium borosilicate (BS) and alumophosphate (AP) glasses, which are important for storing radioactive wastes. The glass compositions are given in Table 1. Equimass substitution of cesium for sodium is connected with growth of the sample activity level. The glasses were synthesized in a glassmaking (silite) furnace at temperatures of 900-1000°C (AP) and 1150-1250°C (BS) from analytical reagents. The melts were poured out onto a metal sheet.

For high-quality measurement of EXAFS spectra, the layer thickness should be $x \cong 2.3/\mu$, where μ is the mass coefficient of atom absorption. Since the matrix containing the element studied consisted of atoms absorbing, to some extent, x-radiation, to obtain an EXAFS spectrum with good resolution the layer thickness differed from the value obtained from the above expression by 10 to 40%. The amplitude of oscillations nearest to the absorption edge was used as a figure of merit.

Samples for EXAFS experiments were prepared in the following way. Glass was crushed to powder in an agate mortar. Then the fine powder fraction (less than 100 μm) was separated in a tube with distilled water and deposited on a mitrocellulose filter by forcing the suspension through the filter with a water-jet pump. The resultant layer was homogeneous over the substrate filter area without inclusions of large particles. Then the layer was air dried. The layer was fixed to the substrate by adding a small amount of PVA adhesive to the water with glass powder. A sample prepared in this way was used in subsequent measurements.

X-ray spectra of the Cs absorption L_3 edge were measured with a laboratory EXAFS spectrometer manufactured at the Solid-State Institute, Latvian University (Riga, Latvia) on the basis of an x-ray DRON-3M diffractometer [5]. BSV-29 and BSV-25 x-ray tubes with different anticathodes (Cu, Cr) were used as x-radiation sources. The width of the radiation spot of the tubes was not more than 0.4 mm, which ensured a spot projection width of less than 40 μm at a radiation take-off angle of 3-6°. This provided an acceptable resolution of the spectrometer ($\cong 3$ eV). The material for the anticathode of the x-ray tube was selected to ensure consistency of the energy of the absorption L-jump of the element studied and the energy distribution maximum of the braking radiation of the tube.

X-radiation was focused by the Johann system with a plate of crystalline α -quartz [1011], 40×10×0.2 mm, as a curved crystal monochromator. The crystal was focused on the input slit of the detector by varying the curvature radius of the crystal at the absorption edge of the element studied. During measurement of the spectrum the crystal curvature remained constant. Radiation defocusing was insignificant and the spectrometer resolution over the whole spectral length ($\Delta E \cong 600-800$ eV) remained constant and the radiation intensity varied within 10% of its average value.

The intensity of monochromated radiation without a sample was about 10^4-10^5 pulse/sec in the energy range of 5-12 keV. The energy resolution of the EXAFS spectrometer was $\Delta E_{1/2} = 3$ eV.

The absorption coefficient was measured by a transmission procedure. A sample was placed in front of the input slit of the detector. The absorption coefficient $\mu(E)$ was determined from the results of successive measurements of x-radiation intensity without (I_0) and with (I) the sample in two scans of the spectrum. The total measuring time of one spectrum was 6 to 24 hours.

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TABLE 1. Compositions of the Glasses Studied

Glass	Component content, wt. %					
	Na ₂ O	CaO	Al ₂ O ₃	B ₂ O ₃	SiO ₂	P ₂ O ₅
BS-1	25	5	—	20	50	—
BS-2	20	10	—	20	50	—
BS-3	15	15	—	20	50	—
BS-4	10	20	—	20	50	—
AP-1	18	10	21	—	—	51
AP-2	15	12.5	21	—	—	51.5

Isolation of the EXAFS components from the absorption spectra was carried out by the standard procedure [6]. The background $\mu_B(E)$ was found from the pre-edge spectral region (100 eV from the edge), which was then approximated by Victorine's law:

$$\mu_B(E) = \frac{A}{E^3} + \frac{B}{E^4},$$

where A and B are constants determined by the least-squares method. Then $\mu_B(E)$ was extrapolated into the energy region beyond the absorption edge and subtracted from the experimental spectrum. The atomic absorption coefficient $\mu_0(E)$ in the region beyond the absorption edge was found by approximation with a second-power polynomial and then refined using a cubic spline. The EXAFS component $\chi(k)$ was defined by

$$\chi(k) = (\mu - \mu_B - \mu_0)/\mu_0,$$

where $k=(E - E_0)^{1/2}$ is the photoelectron wave vector; $E - E_0$ is its energy; E_0 is the reference point for the photoelectron energy. The contributions of photoelectron scattering processes in the first and second coordination spheres to the experimental spectrum were separated by the Fourier filtration method.

In the single-scattering approximation the relation between the amplitude of EXAFS oscillations and the wave vector k of the photoelectron knocked out by an x-radiation quantum is determined as follows:

$$\chi(k) = \sum_i \frac{N_i S_{0i}^2}{k R_i^2} f_i(\pi, k) e^{-2\sigma_i^2 k^2} e^{-2R_i/\lambda(k)} \sin\left(2kR_i + \varphi_i(k) + \frac{2R_i \Delta E_{0i}}{7.62k}\right),$$

where N_i is the coordination number of the i -th sphere; R_i is the radius of the i -th coordination sphere; σ_i is the Debye-Waller factor; S_{0i}^2 is the scale factor, including the multielectronic effects; $\lambda(k)$ is the photoelectron mean free path in inelastic scattering; $f_i(\pi, k)$ is the amplitude of photoelectron backscattering by the ambient atoms; $\varphi_i(k)$ is the phase shift induced by the central and scattering atoms; ΔE_{0i} is the correction to the absorption edge and phase shift values.

The amplitude and phase shift evaluated in the spherical wave approximation and used in this study were taken from [7]. The photoelectron mean free path was approximated by the relation $\lambda(k)=k/\Gamma$, where Γ is the state width, which depends on the ground and final state widths, instrumental resolution and interaction of the photoelectron with the medium and the nearest surroundings.

Structural information can be obtained from EXAFS spectra by their simulation. In this case, coincidence of experimental and simulated curves is a criterion for correctness of the structural data. However, the large number of parameters that are varied in simulation (usually 3 to 20) makes this process the most laborious. To accelerate the process of "fitting" and refining the structural values, optimization methods may be used. In this study Levenberg-Marquardt's modified conventional minimization method was used [8-10].

In Fig. 1 experimental cesium absorption L_3 -edge spectra in BS and AP glasses are shown. Close spacing of the cesium L_3 - and L_2 -edges (5011 and 5358 eV, respectively) prevents recording of the EXAFS spectra in a wide energy range. Furthermore, the considerable mobility and large radius of cesium ions, which result in a very loose first coordination sphere and a large value of the Debye-Waller factor, have a great effect on the quality of the data. It is known that, like other alkali ions, cesium in glass is a grid modifier [11]. The large radius of the cesium ion results in large values of the coordination number in oxygen in the first coordination sphere.

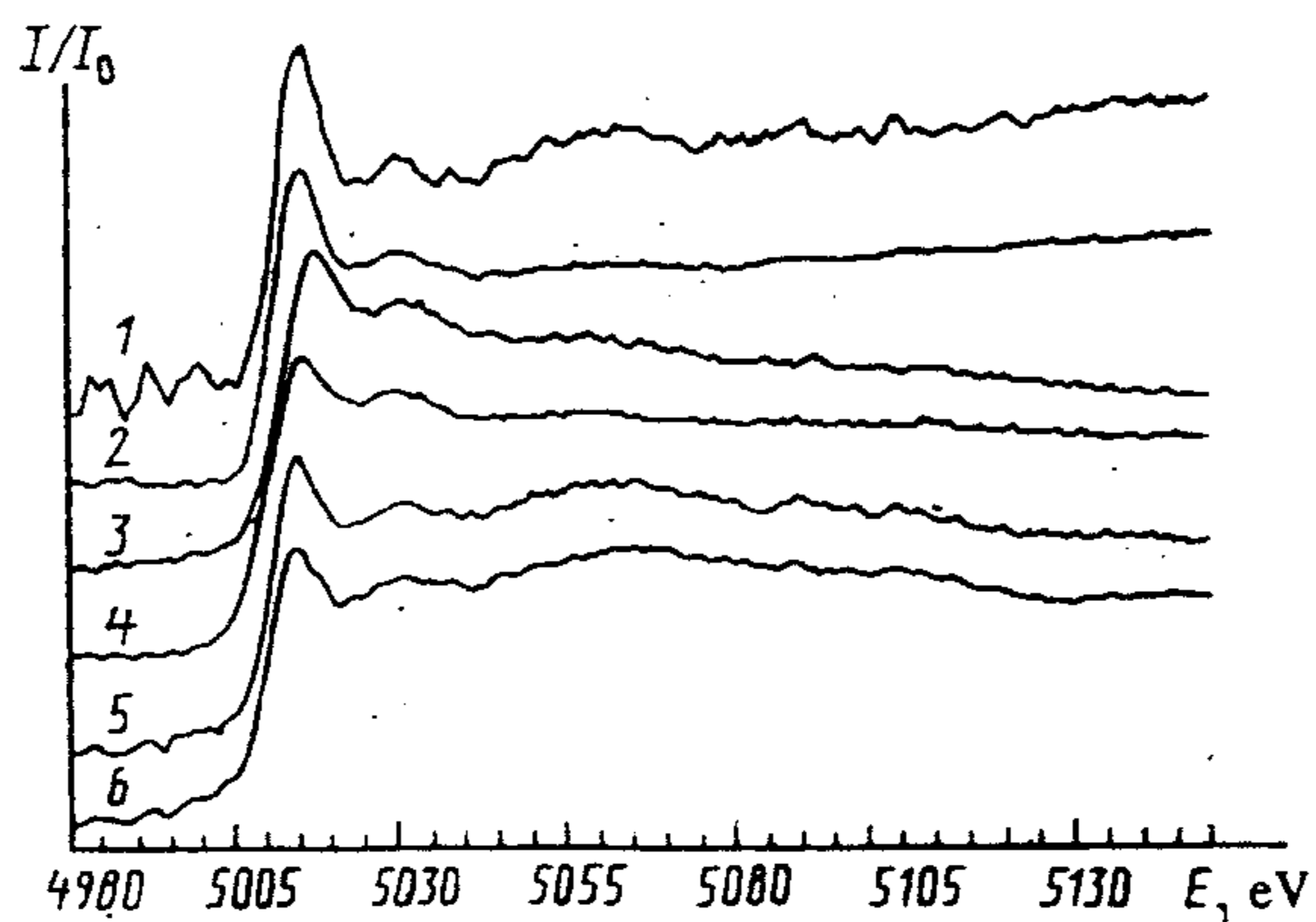


Fig. 1. Cesium absorption L_3 -edge spectra in sodium BS and AP glasses: BS-1 (1), BS-2 (2), BS-3 (3), BS-4 (4), AP-1 (5), and AP-2 (6).

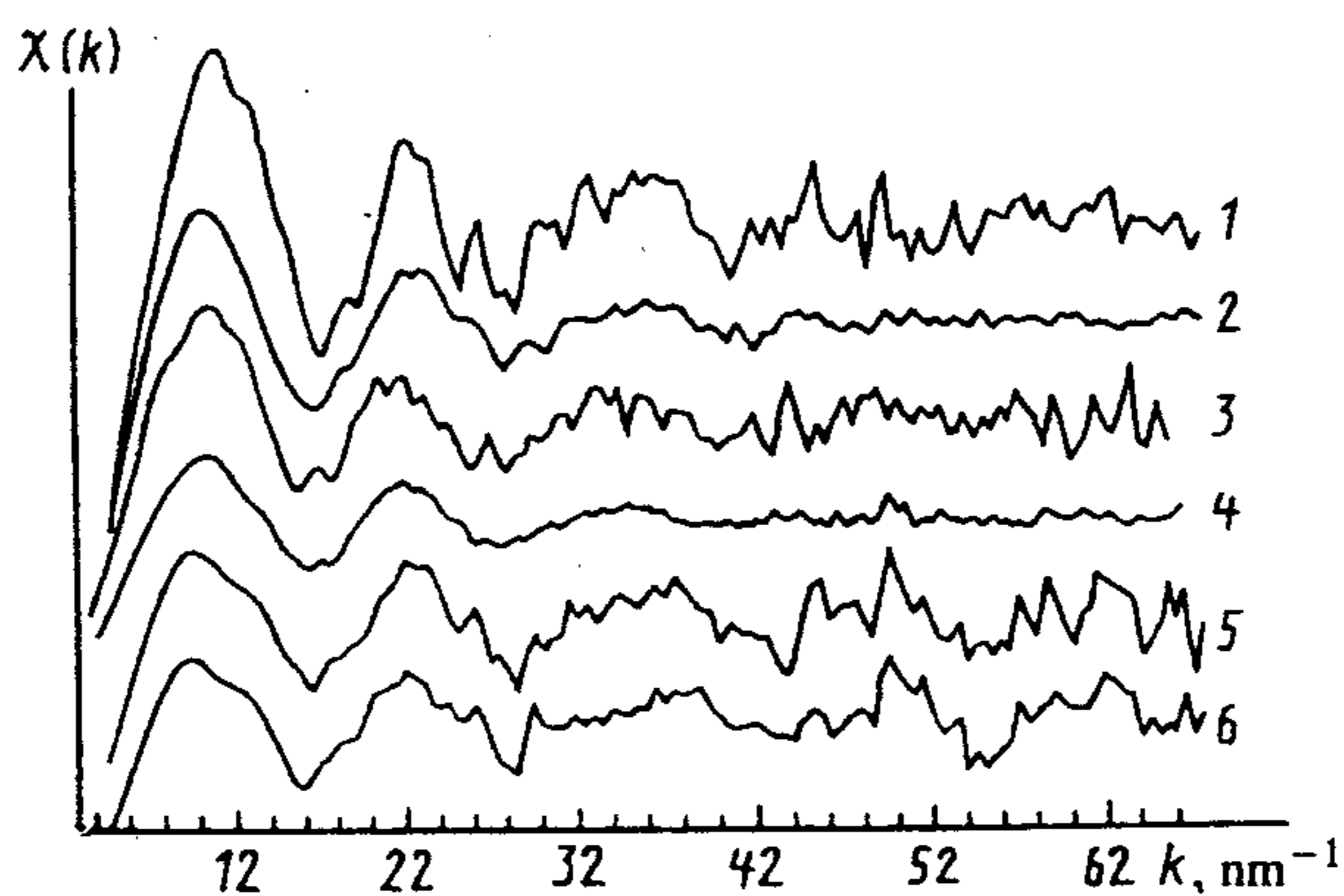


Fig. 2. Cesium EXAFS L_3 -edge spectra in glasses. Designations are the same as in Fig. 1.

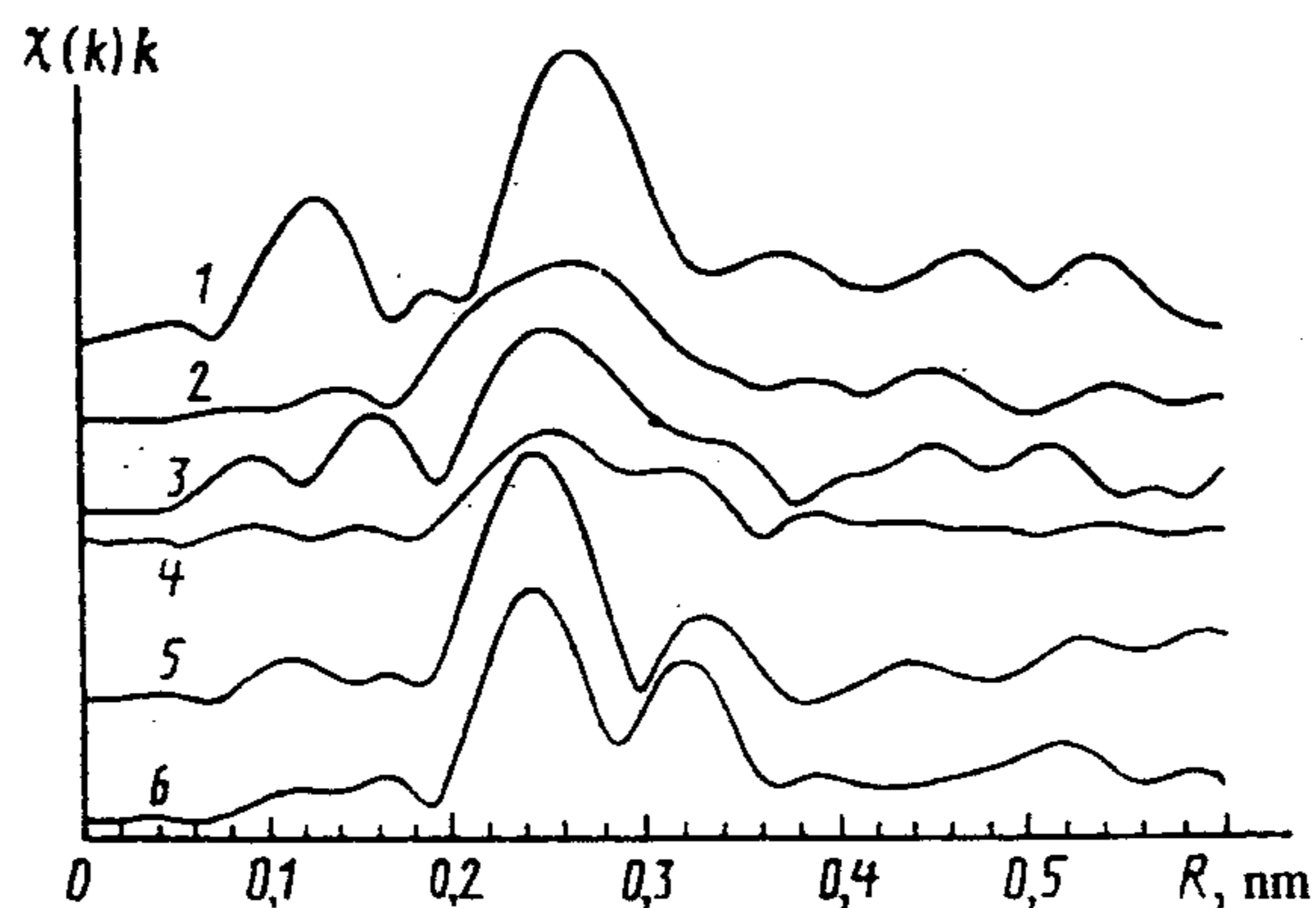


Fig. 3. Cesium L_3 -edge Fourier transforms $\chi(k)k$ in glasses. Designations are the same as in Fig. 1.

In Figs. 2 and 3 EXAFS spectra $\chi(k)$ and their Fourier transforms (FT) are shown. Intense oscillations of the cesium atoms and the disordered structure of the glasses result in smearing of the spikes from the distant coordination spheres. Therefore, in reality, only the spikes located in the region of 0.2 to 0.4 nm can be analyzed. In Fig. 4 examples of experimental

TABLE 2. Simulation Data for EXAFS Spectra in Cesium-Containing Glasses

Glass	Bond	NS_0^2	$R, \text{\AA}$	$\sigma^2, \text{\AA}^2$	$\Gamma, \text{\AA}^{-2}$	$\Delta E_0, \text{eV}$
BS-1	Cs—O	4,8	3,26	0,026	0,17	-4,65
	Cs—Si	0,5	3,31	0,002	0,17	-28,38
BC-2	Cs—O	3,1	3,16	0,039	0,20	-3,65
	Cs—Si	1,7	3,44	0,049	0,20	-12,91
BC-3	Cs—O	2,8	3,10	0,022	0,19	-4,67
	Cs—Si	1,5	3,45	0,031	0,19	-14,31
BC-4	Cs—O	2,2	3,13	0,022	0,29	-4,13
	Cs—Si	1,8	3,42	0,020	0,29	-13,22
AP-1	Cs—O	5,8	3,09	0,008	0,55	-2,28
	Cs—P	4,0	3,55	0,021	0,55	-12,69
AP-2	Cs—O	5,9	2,99	0,001	0,96	-0,78
	Cs—P	5,5	3,56	0,001	0,96	-12,30

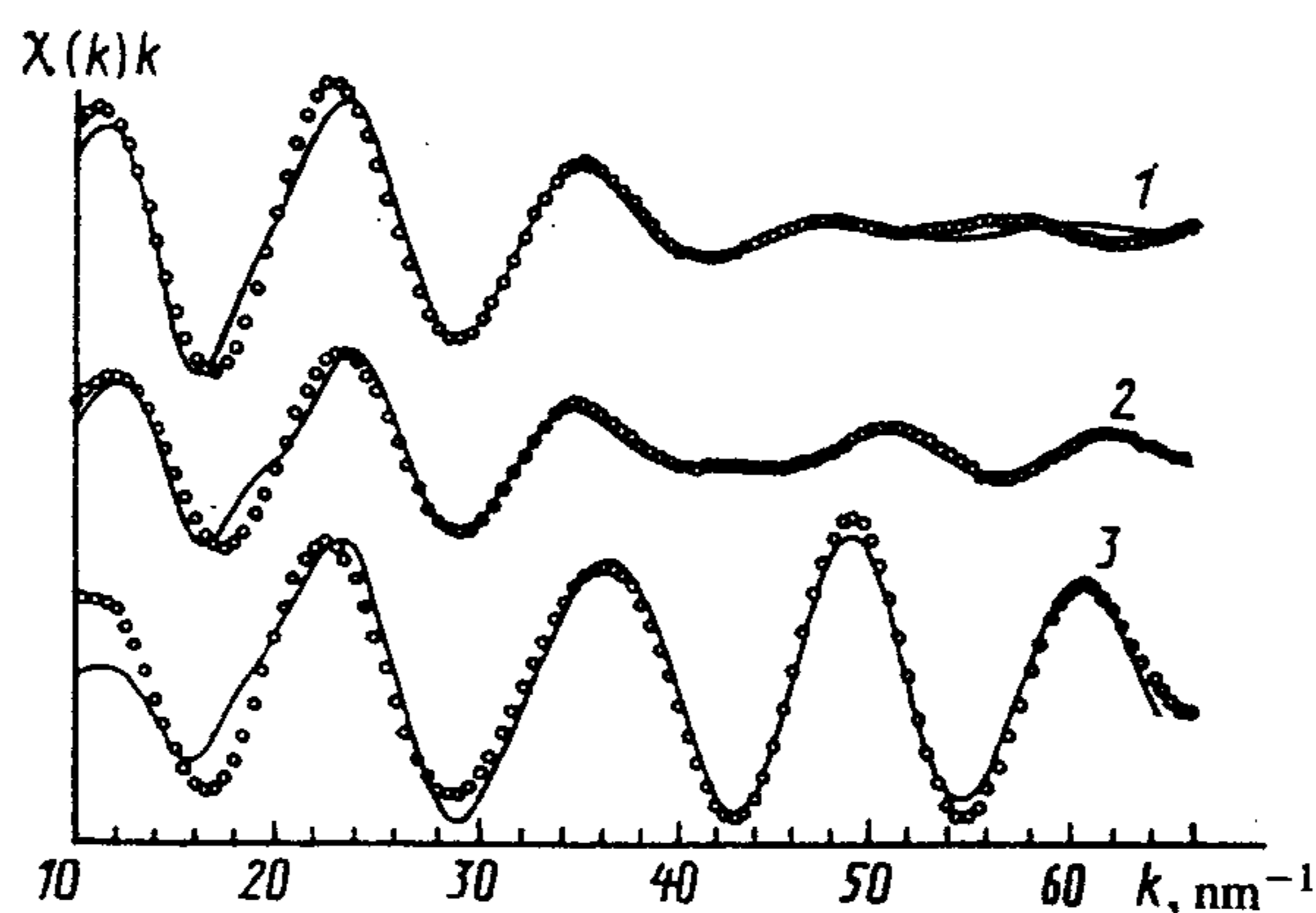


Fig. 4. EXAFS $\chi(k)k$ components of the Cs absorption L_3 -edge from the first coordination sphere in glasses. BS-2 (1), BS-4 (2), AP-1 (3). Circles) experiment; solid line) prediction.

and predicted contributions from spikes located in the region of 0.2 to 0.4 nm are shown, and in Table 2 values of parameters obtained for all the glasses studied are given. From these data it may be concluded that in all the glasses considered the cesium ions are surrounded by oxygen atoms from silicon-oxygen and phosphorus-oxygen polyhedrons. The presence of silicon atoms in BS glasses and phosphorus atoms in AP glasses in the second coordination sphere was also detected (Table 2). It should be mentioned that for AP glasses the average Cs-O distance and the Debye-Waller factor are smaller than those for BS glasses, which is manifested by a decrease in the FT spike half-widths and a shift of their maxima. Furthermore, the effect of decrease in the Debye-Waller factor in AP glasses, resulting in less intensive attenuation of EXAFS oscillations, is noted (Fig. 4).

At small cesium concentrations the mean coordination number of cesium ions referred to oxygen in the first sphere is about 8, and as the Cs_2O concentration increases, it goes down to about 6 in BS glasses. Unlike BS glasses, for AP glasses no definite conclusion can be drawn (Table 2). It should be stressed that the other parameters of EXAFS spectra of BS glasses depend on their composition in a complex manner, which can be ascribed to the impact of boron coordination transitions on the structural net of the glass and redistribution of cesium ions between boron-oxygen clusters with three- and four-coordinated boron atoms.

Equimass substitution of Cs_2O for Na_2O in AP glasses has no noticeable effect on the cesium coordination number referred to oxygen, but a marked decrease of the Cs-P distance in the second coordination sphere is observed (Table 2).

Analysis of EXAFS spectra has not confirmed the existence of metallic type Cs-Cs bonds or Cs-Cs bonds through oxygen (Cs-O-Cs) in the glasses studied. This suggests that the development of cesium atom or ion clusters or cesium-oxygen polyhedron clusters is not characteristic of the glass composition range studied and cesium ions are far apart. Consequently, in the glasses studied, microregions with higher local concentrations of cesium ions do not appear in noticeable amounts and in the presence of cesium radionuclides there is no danger of radiation field power fluctuations arising or the resultant local heating, which can bring about glass crystallization and radionuclide dissipation in the environment.

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