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There is limited information concerning the structural position of cobalt ions in oxide glasses. It has been shown by optical [1], EPR [2], and IR [3] spectroscopy and wide-angle x-ray scattering (WAXS) x-ray diffraction [4] that Co^{2+} ions can be in a tetrahedral or octahedral oxygen environment in glasses. The purpose of the present paper is a study of the state and distribution of cobalt atoms in sodium borate and sodium borosilicate glasses and in borosilicate glasses of complex composition by extended x-ray absorption fine-structure (EXAFS) spectroscopy.

In the present paper, we studied the structural position of cobalt atoms in glasses and crystalline specimens of the following series:

1. $(100 - x)(\text{Na}_2\text{O} \cdot 2\text{B}_2\text{O}_3) - x\text{CoO}$ for $x = 10, 20, 30, 40, 50$, and 100%;
2. $(30 - x)(\text{Na}_2\text{O} \cdot 20\text{B}_2\text{O}_3 \cdot 50\text{SiO}_2 \cdot x\text{CoO}$ for $x = 10$ and 20%;
3. $(25 - x)\text{Na}_2\text{O} \cdot 15\text{CaO} \cdot 5\text{MgO} \cdot 4\text{Al}_2\text{O}_3 \cdot 6\text{B}_2\text{O}_3 \cdot 45\text{SiO}_2 \cdot x\text{CoO}$ for $x = 5, 10, 15, 20$, and 25%.

All compositions are expressed in mass %.

The glasses were melted at 1150°C in a Silit (SiC) furnace from analytical-purity- or cp-grade reagents. The melts were poured onto a metallic sheet. The specimens were ground in an agate mortar.

The EXAFS spectroscopic method, implemented with a serially manufactured DRON-3M x-ray diffractometer, was used to investigate the spatial distribution of cobalt. A spectroscopic attachment [5] made it possible to retain the monochromator crystal on the axis of the goniometer and bend it along the cylindrical surface for focusing of monochromatized radiation by Johann's method onto the inlet slit of the detector (slit size 0.05 mm).

The monochromator crystal was a 0.2-mm-thick crystalline α -quartz wafer cut along the $[10\bar{1}1]$ plane. The x-ray radiation source was a BSV 29-Mo bremsstrahlung tube with focus width 0.4 mm. With electric power 1 kW fed to the tube, the intensity of the zero beam of monochromatized radiation in the region of the K jump of Co was 10^5 counts/sec in the energy width $\Delta E \approx 6$ eV. With exposure 50-100 sec onto the point, it was possible to obtain EXAFS spectra with signal-to-noise ratio 10^3 , adequate for machine processing. The EXAFS spectra were measured in the energy range up to 600 eV beyond the K absorption edge of cobalt by

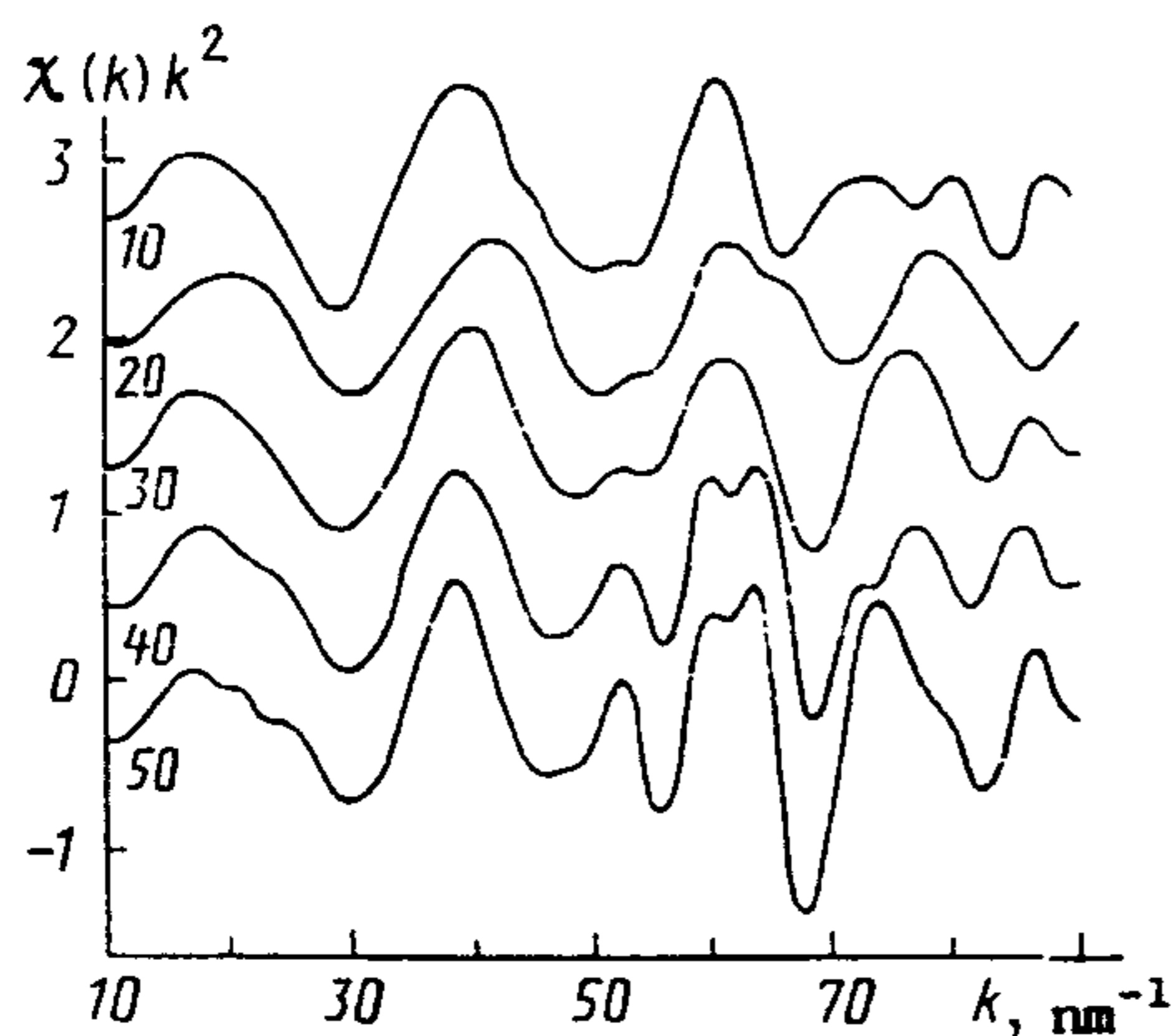


Fig. 1. EXAFS spectra of $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{CoO}$ -system specimens. The numbers at the curves correspond to the CoO content in the specimens.

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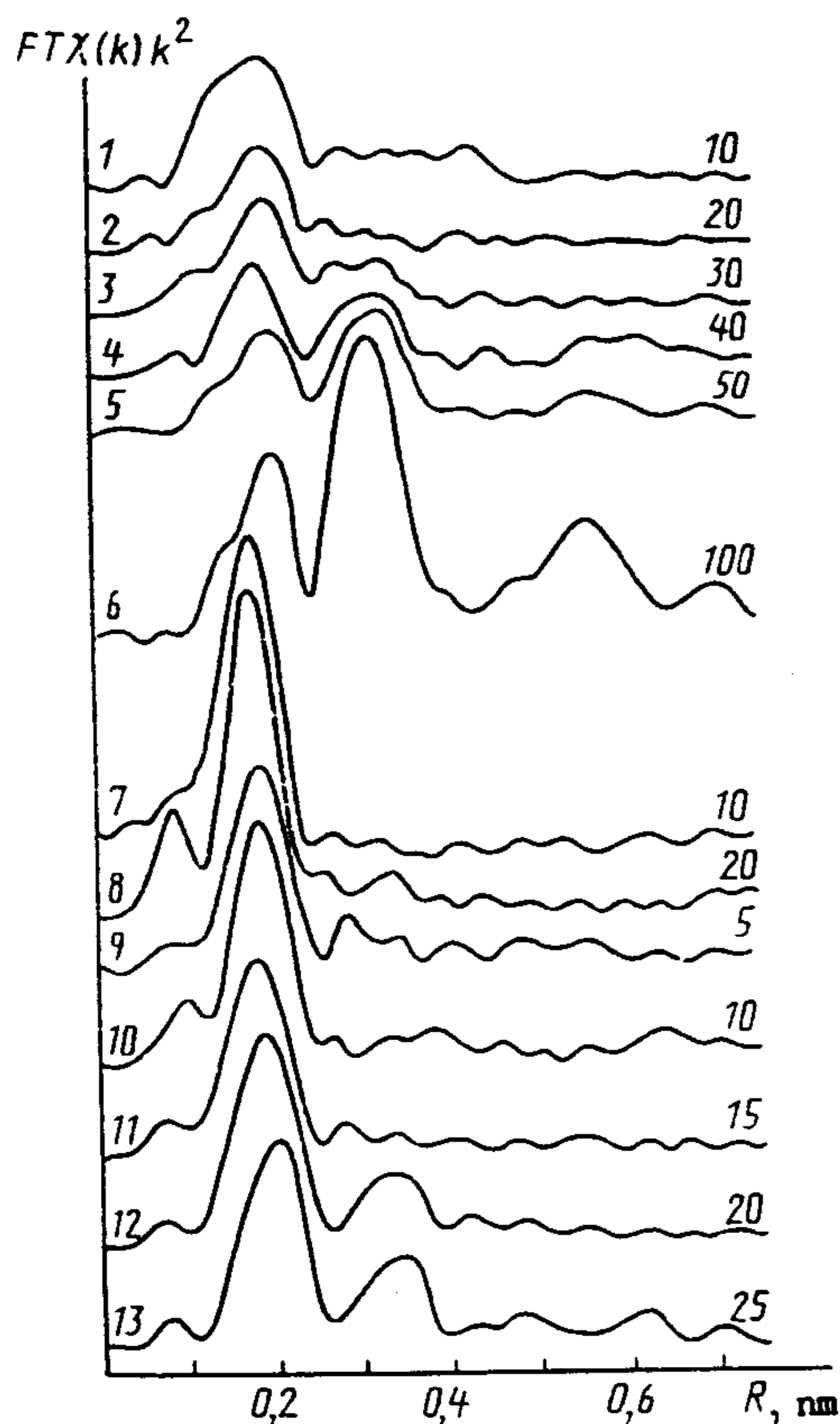


Fig. 2. Fourier transforms of EXAFS spectra of Co K edge in specimens of series 1 (1-6), 2 (7, 8), and 3 (9-13). The numbers to the right of the curves are the values of x .

twofold scanning. The intensity of the zero beam was measured during first scanning, and the intensity of the beam having passed through the specimen was measured during second scanning. Primary information was collected, the spectra were processed and modeled with BK-0010 and IBM PC/AT computers. The obtained spectra were processed by the standard method described in [6] and [7]. The backscattering amplitudes and phases calculated with an approximation of spherical waves in [8] were used in modeling.

The EXAFS spectra of the $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{CoO}$ -system specimens are shown in Fig. 1, and their Fourier transforms are shown in Fig. 2 (curves 1-6). The first peak in all the presented radial distributions corresponds to the Co-O bond in the first coordination sphere. At $x > 20$ there is an increase of the amplitude of the second coordination sphere, and at $x \geq 40$ more-distant coordination spheres appear. A comparison of the spectra of the specimens of the three-component system with the spectrum of c-CoO ($x = 100$) (Fig. 2, curve 6) indicates that the glass crystallizes at CoO concentrations greater than 30%.

For quantitative analysis of the specimens, we modeled the EXAFS oscillations of the first and second coordination spheres of each specimen. An example of least-squares curve fitting for the specimen with $x = 50$ of series 1 is shown in Fig. 3.

In modeling of the first sphere, we obtained two Co-O distances corresponding to two different types of Co^{2+} environment, namely, tetrahedral CoO_4 with distance $r_t \approx 0.202$ nm and octahedral CoO_6 with distance $r_o \approx 0.215$ nm. The scatter of the distances r_t and r_o in different specimens of this series was ± 0.005 and ± 0.004 nm, respectively, which cannot be explained as an experimental error because in our case the Co-O distance was determined with precision of ± 0.001 nm. The obtained result suggests that a change of the CoO concentration in the matrix leads to different distortion of the tetrahedral and octahedral oxygen complexes of cobalt.

In modeling of the second coordination sphere, we also obtained two distances corresponding to Co-Co bonds through the edge of the oxygen polyhedron: $r_{oo} \approx 0.300$ nm ($\text{CoO}_6-\text{CoO}_6$) and $r_{ot} \approx 0.308$ nm ($\text{CoO}_6-\text{CoO}_4$). The scatter of the distances, analogous to that considered above, was ± 0.003 nm in the second coordination sphere.

Fourier transforms of the EXAFS spectra of cobalt in specimens of series 2 are shown in Fig. 2 (curves 7 and 8). Only the first coordination sphere is well resolved in the spectra

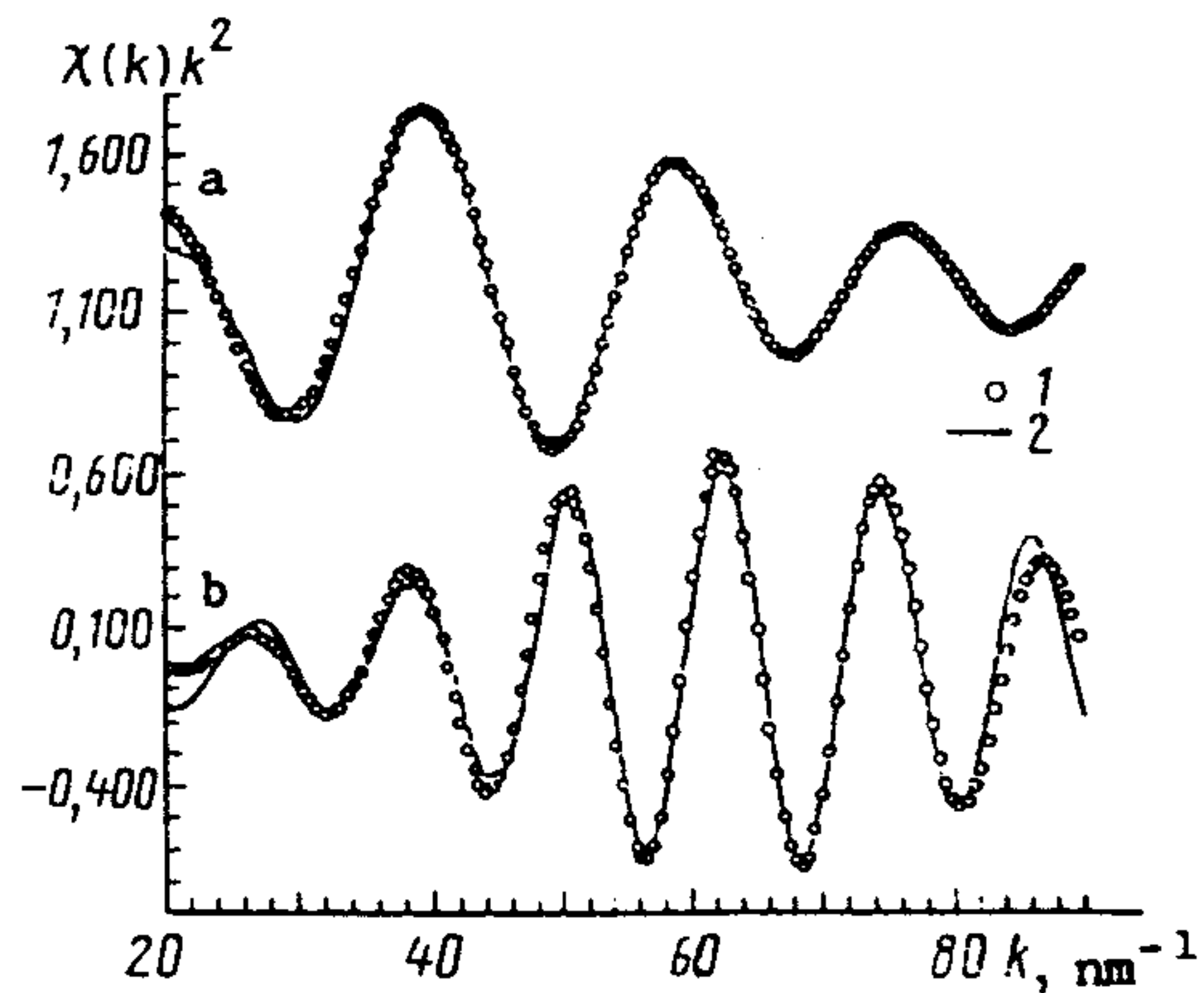


Fig. 3. Example of least-squares curve fitting of the first (a) and second (b) coordination spheres of cobalt (1 denotes the experimental values, and 2 denotes the calculated values).

of both vitreous specimens, and at $x = 10$ there is one peak corresponding to the Co-O distance $r_t \approx 0.197$ nm in the CoO_4 tetrahedron. A similar picture was also observed in the spectrum of the glass with $x = 20$, but here the structure of the first peak was more complex (Fig. 2, curve 8).

The Fourier transforms of the EXAFS spectra of the K edge of cobalt in the multicomponent glasses are shown in Fig. 2 (curves 9-13). An increase of the CoO concentration in glasses of series 3 led to the appearance and increase of the amplitude of the peak of the second coordination sphere and an increase of the average Co-O distance in the first sphere. Similarly to the three-component system, distances corresponding to tetrahedral $r_t \approx 0.198$ nm and octahedral $r_o \approx 0.212$ nm complexes were observed in the first series of glasses of series 3. The scatter of the distances was ± 0.005 and ± 0.006 nm, respectively. In modeling of the second sphere, we also observed two distances between cobalt ions located in the complexes connected through the edge, namely, $r_{oo} \approx 0.297$ nm ($\text{CoO}_6\text{-CoO}_6$) and $r_{ot} \approx 0.315$ nm ($\text{CoO}_6\text{-CoO}_4$). The scatter of the distances was ± 0.003 and ± 0.002 nm, respectively.

In all the considered cases, Co-Co metallic bonding was not observed.

As shown by computer modeling, the dissolution of CoO in glass of tetraborate composition leads to the incorporation of Co^{2+} ions in the structural network in two ways: Some of the Co^{2+} ions occupy tetrahedral positions and are incorporated in the boron-oxygen network; the rest of the Co^{2+} ions are located in octahedral vacancies in the position of the network modifier. In both cases, the Co-O distances agree with the data presented in [9].

Essentially only four-coordinate cobalt exists in the glasses of the $\text{Na}_2\text{O-B}_2\text{O}_3\text{-SiO}_2\text{-CoO}$ system that were studied: CoO_4 tetrahedrons are incorporated in the structural network of the glass, which agrees with the conclusions of [4], although at high CoO concentrations ($\geq 20\%$) the CoO_4 tetrahedrons may be strongly deformed, as is evident from the complex structure of the first peak of the Fourier transform of the EXAFS spectrum of the glass with $x = 20$ of series 2 (Fig. 2, curve 8).

In multicomponent borosilicate glasses, just as in sodium borate ones, CoO manifests properties of both a network former and a modifier. As was already noted, the peak corresponding to the second coordination sphere has two components: r_{oo} and r_{ot} . From Fig. 2, it is evident that the ratio of these components varies in relation to the composition of glasses of series 3 in a complex way: Joining of octahedrons predominates in glass with $x = 5$, and joining of tetrahedrons and octahedrons predominates in glasses with $x \geq 20$. Small additions of CoO (instead of Na_2O) to borosilicate glass probably do not result in a significant change of the structure of the matrix glass; the Co^{2+} ions occupy octahedral vacancies in the boron-silicon network without significant interaction with it. With an increase of the concentration of CoO in the glasses, Co^{2+} strives to form its own oxygen environment with a relatively low coordination number, about 4.

On the basis of the amplitudes of the peaks corresponding to the second and subsequent coordination spheres, we can assess the distribution of the atoms being studied in the glasses: the greater the amplitudes of these peaks with respect to the amplitude of the first peak, the stronger the interaction of the complexes of the given atoms between themselves. As is evident from Fig. 2 (curves 9-13), the cobalt atoms are distributed most homogeneously in glasses of series 3 with $x = 10$ and 15, where the peak of the second coordination sphere is virtually absent. Homogeneous cobalt distribution also occurs in glasses of series 2 (Fig. 2, curves 7 and 8).

In the borosilicate glasses that we studied (series 2 and 3), the parameter ψ_B [10] is greater than unity; therefore, such glasses do not tend to undergo phase separation. Therefore, there is no question of the distribution of Co between coexisting phases (or regions of chemical order preceding phase separation). Otherwise, the interpretation of the experimental data cannot be completely unambiguous.

Thus, the Co was in tetrahedral and octahedral coordinations in the sodium borate and multicomponent borosilicate glasses. The oxygen polyhedrons were strongly distorted and could be joined to each other through edges ($\text{CoO}_6\text{-CoO}_6$ and $\text{CoO}_6\text{-CoO}_4$). A decrease of the Na_2O content in the glass led to an increase of the number of Co atoms in the tetrahedral environment, which was manifested in a decrease of the average Co-O distance in the first coordination sphere. In the sodium borosilicate glasses with $\psi_B \geq 1$, virtually all the cobalt was four-coordinate.

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