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Alkali effect on Co(II) ions structuring in borate glasses

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The color change of cobalt borate glasses obtained by varying the alkali content in the glass has been investigated by x-ray diffractometry. A good number of spectroscopic studies attributed the change of color to a structural rearrangement of the cobalt ion in the host glass but no direct structural information has been presented to date. We examined three cobalt borate glasses containing about 5% in weight of CoO and different K₂O contents (about 15%, 22%, and 29% in weight). Their radial distribution functions were compared with those of suitable cobalt-free potassium borate glass matrices and difference distribution curves obtained. Analysis of these curves allowed a quantitative description of the cobalt environment in terms of tetrahedral \rightleftharpoons octahedral structural rearrangements.

INTRODUCTION

Glasses containing cobalt are among the materials which play a major role in the production of colored glasses owing to the attractiveness of their pure blue color. Many studies, mainly optical characterization,¹⁻⁵ have been devoted to these glasses. Nevertheless, the present state of knowledge is characterized by a lack of structural information. Only recently, some x-ray diffractometric⁶⁻¹¹ and EXAFS¹² investigations on the structural characterization of cations in glasses have been published.

Yet, the structural information could be of greater help in clarifying the behavior of Co²⁺ ions in alkali borate glasses. It is, in fact, well known that a decrease of the alkali content in these glasses changes the color from a typical deep blue to a pale pink. Many spectroscopic studies have explained this color shift in terms of a change of the coordination of the cobalt ions from tetrahedral to octahedral by decreasing alkali/boron ratio in the host glass. However, in spite of the substantial agreement in the interpretation of the phenomenon, no direct information has been given about such coordination change. Most studies only refer to direct tetrahedral to octahedral change,^{3,4} but a deeper analysis of the spectra reveals the involvement of some intermediate or defective coordination in the overall process.¹ The fact that octahedral and tetrahedral coordinations are revealed in the same frequency region of cobalt spectra surely accounts for this general lack of quantitative information.¹³

In this paper we report an x-ray diffractometry study on three potassium borate glasses containing about 5% in weight of CoO and different potassium oxide content. The x-ray data were interpreted using the difference curve method already successfully employed in studying the coordination of various cations incorporated in glass matrices.⁶⁻¹¹

EXPERIMENTAL

Samples preparation and analyses

Weighed amounts of pure reagent grade B₂O₃, K₂CO₃, and Co₃O₄ (Carlo Erba) were mixed and ground in an agate

ball mill (Pulverisette 5-FRITSCH), transferred to a Pt-Rd 10% crucible and poured in an electric furnace under normal atmosphere. The temperature was raised from room temperature to 1173 K in 2 h, and then kept constant for 90 min. The melt was cast in a rectangular aluminum mold, annealed at 573 K for 30 min and cooled down by following the thermal inertia of the annealing furnace.

Six glasses were prepared by the above procedure. Three of them contained about 5% of CoO in weight and different alkali content (about 15%, 22%, 29% of K₂O by weight; hereafter referred to as CoBoK15, CoBoK22, and CoBoK29) and three having the same compositions but without cobalt (and hereafter referred to as matrices or BoK15, BoK22, and BoK29). Glass blocks of 4 × 2.5 × 1 cm were finally obtained. The densities were measured using an AE 163 Mettler electronic Westphal balance.

The actual composition of the glasses was obtained by chemical analyses (within $\pm 1\%$) of the samples by atomic absorption spectroscopy and colorimetric titrations.¹⁴ Due to the preparation conditions, presence of cobalt in the Co(III) oxidation state was not expected and analytically not detected. The results, summarized in Table I, are in agreement with the batch weights.

Optical spectra

Slices of approximately 300 μ m were prepared for optical spectra. During the measurements the samples were kept in a closed quartz cell to protect them from air moisture. The 400–700 nm range spectra recorded by a Super Scan 3-Varian spectrophotometer are reported in Fig. 1.

X-ray data collection and treatment

A θ - θ x-ray diffractometer (Rich Seifert and Co.) with horizontal sample was used for data collection.¹⁵ The glasses were put into a cell covered with a mylar foil which avoided atmospheric attack. Intensity data were collected, using Mo-K α radiation from $s = 0.6$ up to $s = 16.6 \text{ \AA}^{-1}$ ($s = 4\pi \sin \theta / \lambda$), at discrete intervals for a total of about 200 points. At least 100 000 counts were collected for each preset point.

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TABLE I. Compositions of the three pairs of potassium borate glasses with and without cobalt atoms expressed in atomic ratios. V_B are the stoichiometric volumes used for x-ray data reduction. μ is the absorption coefficient.

Glass	$d \text{ (g cm}^{-3}\text{)}$	n_B	n_K	n_O	n_{Co}	$V_B \text{ (}\AA^3\text{)}$	$\mu \text{ (cm}^{-1}\text{)}$
BoK29	2.270(2)	1	0.41	1.70	...	39.664	12.30
CoBoK29	2.311(2)	1	0.42	1.75	0.037	41.397	15.90
BoK22	2.162(2)	1	0.29	1.64	...	37.119	9.63
CoBoK22	2.248(2)	1	0.29	1.68	0.034	37.669	13.37
BoK15	2.079(2)	1	0.17	1.59	...	34.279	6.97
CoBoK15	2.163(2)	1	0.17	1.62	0.029	34.624	10.42

The observed intensities were corrected for background, absorption, and polarization and normalized by a semiempirical method.¹⁶

The structure functions $i(s)$ (Fig. 2) were obtained according to

$$i(s) = I_{obs}^{c.u.} - \sum_i n_i f_i^2(s), \tag{1}$$

where $I_{obs}^{c.u.}$ are normalized intensities, n_i are the stoichiometric coefficients of the assumed unit, and $f_i(s)$ are the scattering factors of the species.

Radial distribution functions $D(r)$ were calculated by

$$D(r) = 4\pi r^2 \rho_0 + 2r/\pi \int_{s_{min}}^{s_{max}} si(s)M(s)\sin(rs)ds, \tag{2}$$

where $\rho_0 = [\sum_i n_i f_i(0)]^2/V$ is the average scattering power from the chosen composition unit of volume V , and $M(s)$ is a

modification function⁹ used to minimize the truncation errors in the Fourier transformation. The radial curves of the six glasses are reported in Figs. 3 and 4.

ANALYSIS OF THE RESULTS

Optical spectra

The optical spectra of Fig. 1 are in very good agreement with previously published results on glasses of similar compositions.¹⁻⁵ The CoBoK29 glass shows the highest absor-

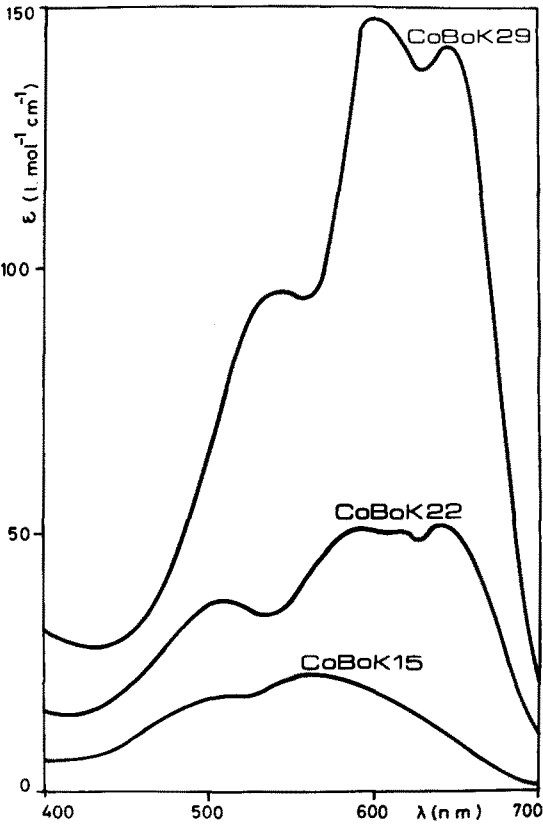


FIG. 1. Molar absorptivity ϵ vs λ for the three investigated cobalt borate glasses.

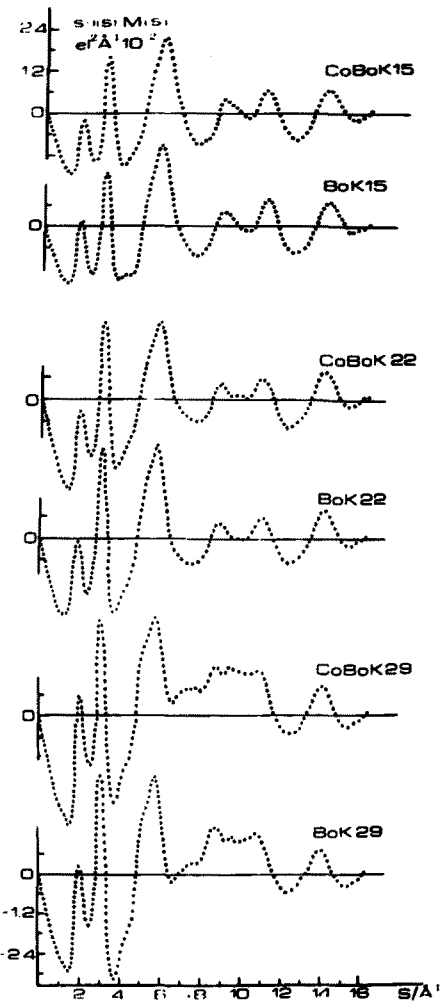


FIG. 2. Experimental reduced intensity functions, $s \cdot i(s) \cdot M(s)$, for matrices (BoK15, BoK22, and BoK29) and for cobalt glasses (CoBoK15, CoBoK22, and CoBoK29).

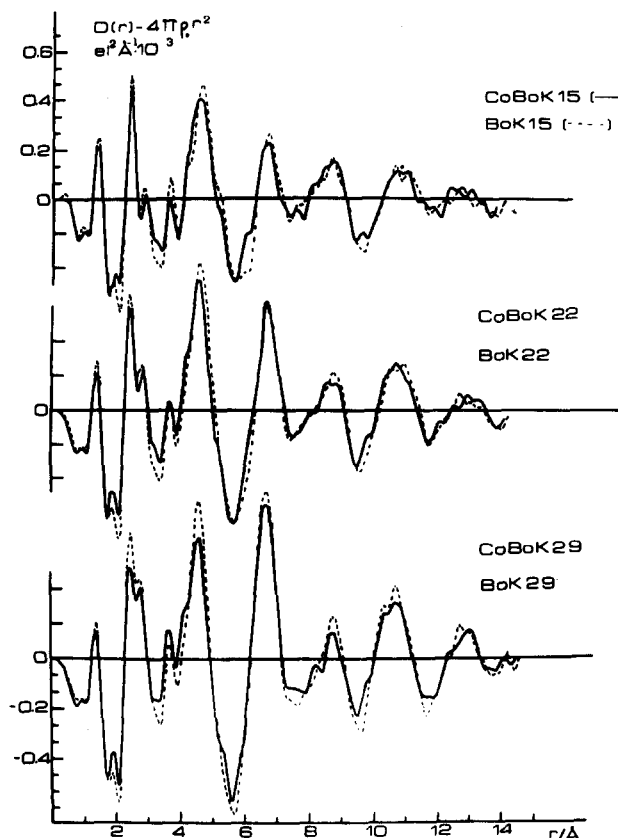


FIG. 3. Radial distribution functions in the differential form, $D(r) - 4\pi r^2 \rho_0$, for the six glasses investigated are shown in the 0–14 Å range.

bance values. The general shape of the spectrum is very similar to that given by Brode¹ for a cobalt potassium borate glass and the absorption maximum, attributed to the $^4A_2 \rightarrow ^4T_1$ transition of cobalt in tetrahedral sites, is split into three maxima at 540, 590, and 640 nm due to spin–orbit coupling. The marked absorbance decrease in going from CoBoK29 to CoBoK22 is indicative of a transition towards a different structural arrangement and the maximum at 510 nm is probably due to the octahedral transition $^4T_1(F) \rightarrow ^4T_1(P)$. Finally in CoBoK15 the spectrum is much flatter and it is very hard to distinguish any definite band.

Inspection of radial curves

For each pair of the radial curves reported in Figs. 3 and 4 the following points can be pointed out: (i) the perfect coincidence of the first peak, due B–O interactions, in each pair of glasses (Fig. 4). The position of the peak increases from 1.42 to 1.44 Å and to 1.45 Å as a consequence of the partial change from triangular to tetrahedral boron coordination by increasing the alkali content¹⁷; (ii) the close similarity of the peak at 2.4 Å (mainly due to O–O pairs within triangular BO_3 and tetrahedral BO_4 units) and at 2.9 Å (Fig. 4); (iii) up to 12–14 Å (Fig. 3) the general shape of the curves is nearly the same for both matrices and cobalt glasses. All this considered we can affirm that the structure of the matrices keeps substantially unaltered when the guest cobalt atoms are introduced into them even though minor modifications must occur due to the presence of cobalt ions.

In fact, it can be seen that the cobalt glass curves of Fig. 4 are meaningfully higher than the corresponding matrix curves just in the region between 1.7–2.2 Å, where Co–O interactions are expected to fall. Figure 5 shows the difference curves obtained by subtraction of the radial functions of the matrices from those of the corresponding cobalt glasses.

Analysis of the difference curves

The experimental radial function $D(r)$ of Eq. (2) is the sum of the partial function $D_{ij}(r)$ relative to all the atom

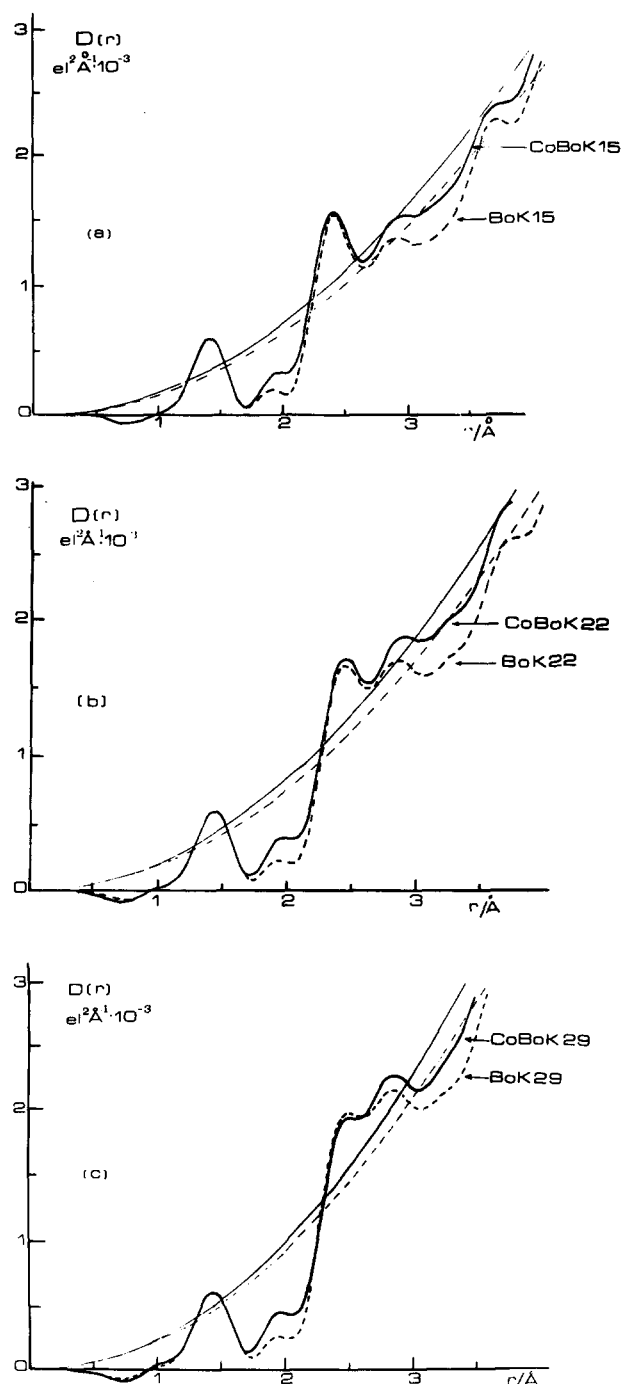


FIG. 4. (a), (b), and (c) radial distribution functions, $D(r)$, of cobalt glasses (solid lines) compared to the $D(r)$ functions of the matrix (dotted lines). The radial curves have been normalized to a unit of volume containing one boron atom (V_B in Table I).

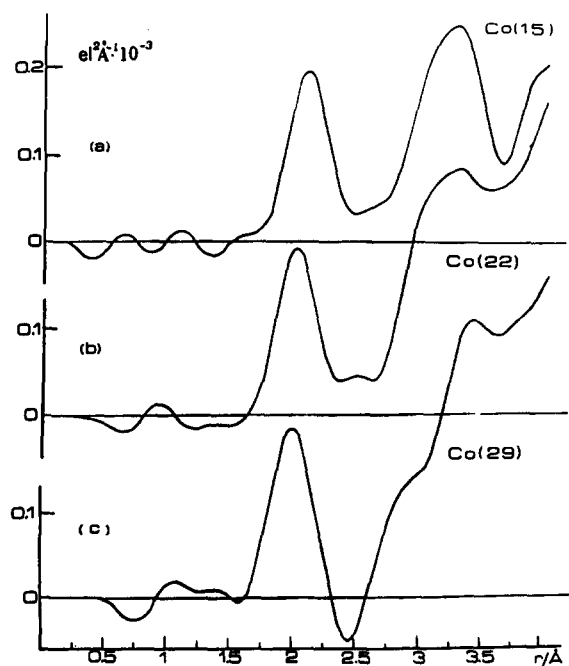


FIG. 5. Radial distribution difference curves $\Delta D(r)_{\text{expt}}$ [see Eq. (4)] for the cobalt glasses. Note the change of the ordinate scale with respect to Fig. 4.

pairs i - j present in the glass:

$$D(r) = \sum_i n_i \sum_j D_{ij}(r), \quad (3)$$

where the summations are taken over the composition units to which the intensities are normalized. The difference curves given in Fig. 5 can be interpreted in the following way. In the glass matrix (M) some x type of guest atoms (cobalt) have been introduced to give the cobalt glass (G). The two samples G and M have compositions such that $n_i^G = n_i^M$ when $i \neq x$. If we now assume that introducing the cobalt atoms does not affect the preexisting network, then $D_{ij}^G(r) = D_{ij}^M(r)$ when i and j are different from x and we have

$$\begin{aligned} \Delta D(r)_{\text{expt}} &= D^G(r) - D^M(r) \\ &= n_x \sum_j (2 - \delta_{xj}) D_{xj}(r), \end{aligned} \quad (4)$$

with δ the Kronecker function. The difference curves of Fig. 5, as long as Eq. (4) is valid, are representative of the short range order around the cobalt ions only.

The main feature of the difference curves is given by the Co-O peak which is well defined and nearly symmetric in all the cases. It is centered at 2.08 Å in Co(15) [hereafter Co(x) stands for the difference curve CoBoK x -BoK x] and shifts to 2.02 in Co(22) and to 1.99 Å in Co(29) at the highest alkali concentration. Second sphere interactions around cobalt ions are evidenced by the broad and composite peak around 3-3.3 Å.

A quantitative analysis of the Co-O experimental peaks has been carried by fitting procedures. Calculated theoretical peaks were obtained by Fourier transforming, with the integral expression given in Eq. (2), the $i(s)_{\text{calc}}$ values given by

$$i(s)_{\text{calc}} = \sum_j n_j \sum_{p,q} (2 - p q) f_p f_q \frac{\sin s r_{pq}}{s r_{pq}} \exp(-b_{pq} s^2), \quad (5)$$

where the first summation runs over the number of assumed structural units, and the second over the atoms contained in each structural unit. In this expression, r_{pq} (average distance between atoms p and q), b_{pq} (associated Debye-Waller factor), and N_{pq} (number of terms of the p, q summation which gives the number of atoms q around each atom p) are adjustable structural parameters. The final results are shown in Fig. 6 [(a), (b), and (c)]. The best average structural pa-

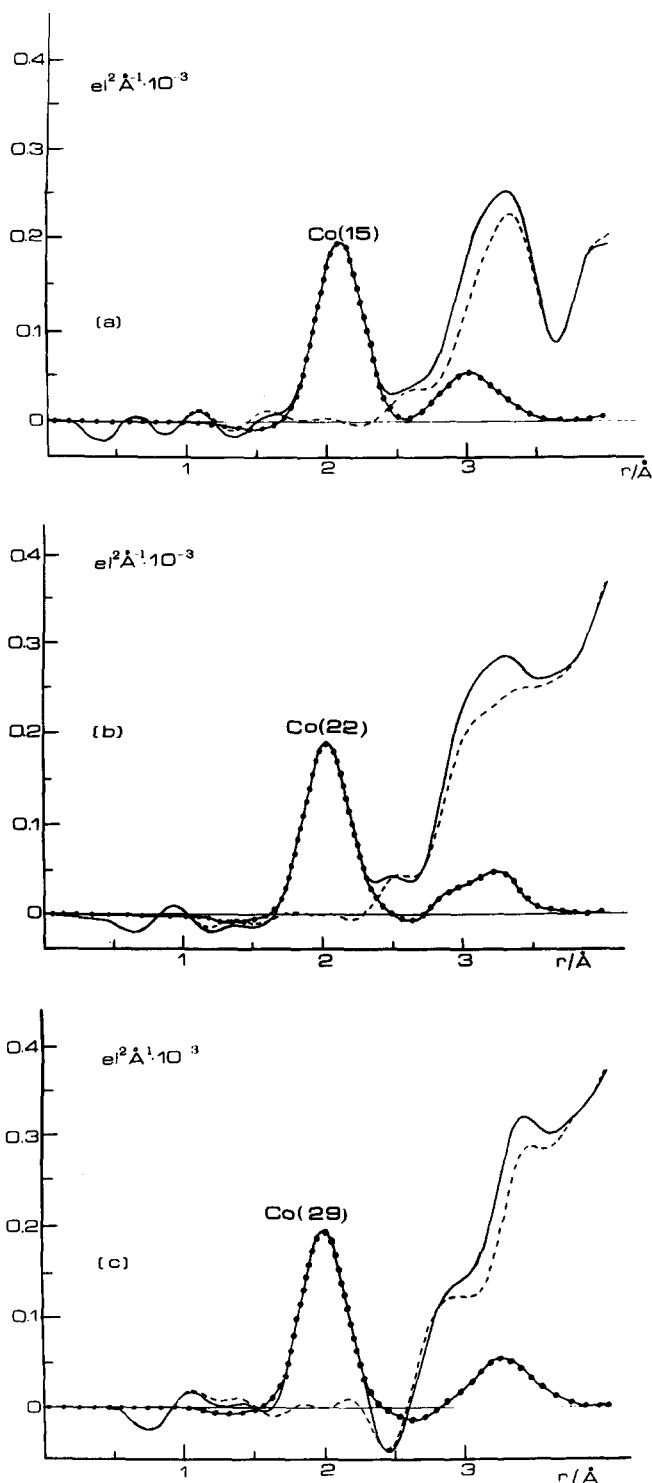


FIG. 6. Curve fitting of the Co-O peaks for Co(15) (a), Co(22) (b), and Co(29) (c) glasses. The sum of the calculated peak shapes $D(r)_{\text{calc}}$ is shown by solid lines and dots and has been drawn by using the parameters of Table II.

rameters obtained are given in Table II. Values in parentheses in Table II indicate the maximum of deviation on the structural parameters beyond which the worsening of the fit becomes evident.

DISCUSSION

The quantitative analysis of Co^{2+} ion coordination carried out through Eqs. (3)–(5), must be considered as correct as far as the structural arrangement of the matrix is not modified by the presence of the cations. In principle, this condition cannot be completely true but it is sufficient, to our purpose, that the assumption is valid up to the distance range involving the first cobalt coordination shell ($r < 2.5 \text{ \AA}$). This range includes first distances within elementary rigid units (BO_3 and BO_4 in our case) of the glassy network which remain unchanged when introducing guest atoms. The most convincing experimental support is given by the peak due to the B–O interaction which appears unaltered in cobalt glasses and in matrices [see Figs. 4(a)–4(c)]. The assumption of “structural similarity” between cobalt glasses and matrices is therefore highly realistic.

Provided the physical assumption is true, it becomes essential to assess the reliability of the structural parameters. The standard deviations of Table II are just coming from the computer fitting procedure. The real uncertainty is probably higher and cannot be exactly evaluated. The experience up to now accumulated,^{6–11,18} indicates that the precision of the method is strongly dependent on the accuracy of the experimental work: the preparation procedure, the alignment of the x-ray apparatus, the counting statistics, and the treatment of the experimental data must be kept rigorously constant. The exact evaluation of all these error sources on the final parameters is very difficult or impossible at all and, above all, the partial validity of the assumption could systematically affect the results. Only further applications of the method and comparison of the results with information from other sources, whenever possible, will give a definite answer to this point. However, some encouraging experimental evidence can be outlined. Figure 4 shows that systematic errors have been minimized since spurious ripples at low r are small and display the same behavior in each pair of glasses. Hence, only minor peaks appear in the 0–1.5 \AA region of the difference curves of Fig. 5, ensuring that system-

atic errors have not seriously affected the real difference peaks. Therefore, even though the real uncertainty cannot be quantified, the obtained trend for the structural parameters is meaningful.

All this considered the results of Table II indicate longer Co–O distances and increasing coordination numbers by decreasing the alkali content. A Co–O distance of 1.99 \AA , with cobalt in tetrahedral configuration, has been found in C_3O_4 .¹⁹ Longer Co–O distances are expected for cobalt in octahedral configuration on the basis of ionic radii (2.13 \AA).²⁰ Thus, the value of 1.99 \AA found in Co(29) strongly suggests a cobalt tetrahedral configuration. The Co–O distance shifts to 2.02 \AA in Co(22) and 2.08 \AA in Co(15) indicating a structural rearrangement towards cobalt octahedral configuration.

The same conclusion of structural rearrangement is reached if we look at the average coordination numbers obtained by the peak area analysis (see Table II). These values closely match the trend of distances. In Co(29) the value of 1.99 \AA obtained for the Co–O distance together with the large absorbance of the optical spectrum strongly suggests the predominance of tetrahedral species. The fit of Fig. 6(c), obtained by setting four oxygen neighbors at 1.99 \AA from the central cobalt atom (only $b_{\text{Co-O}}$ was allowed to vary), is very good and therefore both structural parameters, $r_{\text{Co-O}}$ and $N_{\text{Co-O}}$, point concordantly towards the tetrahedral cobalt coordination.

Peak areas in Co(22) and Co(15) increase to a maximum of about five Co–O contacts in Co(15). Here, in absence of other indications, the peak shape fitting of the Co–O difference peaks can give only the average coordination numbers since letting both $r_{\text{Co-O}}$ and $b_{\text{Co-O}}$ vary freely, more than one combination of octahedral and tetrahedral coordinations can be found to match the experimental difference curves. The choice then was to fix the $r_{\text{Co-O}}$ distances to the values indicated by literature information: i.e., 1.99 and 2.13 \AA for tetrahedral and octahedral distances, respectively. The amounts of tetrahedral and octahedral forms and the temperature factors $b_{\text{Co-O}}$ associated to each $r_{\text{Co-O}}$, were considered as adjustable parameters in the fitting procedure. The final results are reported in Table II and Figs. 6(a) and 6(b). Of course, in view of the uncertainty connected with difference peaks, the estimated percentages of octahedral and tetrahedral forms can be affected by a not negligible error. Nevertheless, within the interpretative scheme assumed

TABLE II. Average structural parameters obtained from the peak shape analysis are given on the left-hand side of the table. The structural parameters and the percentages of the tetrahedral and octahedral forms used for the fits of Fig. 6 are given on the right-hand side. Standard deviations are given in parentheses (see the text).

Glass	Average structural parameters			Model assumed					
				Tetrahedral			Octahedral		
	$r_{\text{Co-O}}$ (\AA)	$b_{\text{Co-O}}$ (\AA^2)	$N_{\text{Co-O}}$	%	$r_{\text{Co-O}}$ (\AA)	$b_{\text{Co-O}}$ (\AA^2)	%	$r_{\text{Co-O}}$ (\AA)	$b_{\text{Co-O}}$ (\AA^2)
CoBoK29	1.99(1)	0.0065(5)	4.0(1)	100(3)	1.99(1)	0.0065(5)
CoBoK22	2.02(1)	0.0032(5)	4.4(1)	80(5)	1.99(1)	0.0025(5)	20(5)	2.13(1)	0.0050(5)
CoBoK15	2.08(1)	0.0057(5)	5.15(10)	43(5)	1.99(1)	0.0045(5)	57(5)	2.13(1)	0.0065(5)

(i.e., fully occupied tetrahedral and octahedral sites and fixed 1.99 and 2.13 Å distances), the estimated percentages clearly indicate the predominant species in each glass.

Finally, an apparent discrepancy between x-ray data and optical spectra has to be mentioned. Assuming only tetrahedral coordination for cobalt in CoBoK29, 80% of this form (see Table II) in CoBoK22 should give an optical spectrum more similar to CoBoK29 than to CoBoK15 in contrast with the experimental results (see Fig. 1). A possible explanation of this inconsistency may be found in an old extensive optical study of Brode.¹ He observed that "...subtraction of either the extreme blue or pink curves from the equilibrium curves indicates that an *intermediate compound* or *partially coordinated complex* must exist between the blue and pink colored forms...". On the basis of the average structural parameters obtained, we can now propose two different explanations of Brode's observation. The "intermediate compound" can be a form having the same structural arrangement but a different optical behavior (the same tetrahedral cobalt coordination, in, let us say, CoBoK29 or CoBoK22, may be subject to different ligand fields). Alternatively, the "partially coordinated complex" suggests the possibility of defective cobalt coordination. Assuming four as a minimum number of oxygen neighbors for the "network former" species (high alkali content), the defective coordination might exist in the "network modifier" octahedral form (low alkali content). From this perspective, we verified that calculations, where the occupancy of the octahedral sites and the 1.99 and 2.13 Å distances were allowed to vary, led to almost equivalent good fits with several different combinations of tetrahedral and "defective-octahedral" struc-

tural arrangements. Both interpretations are realistic and go in the direction of a better agreement between x-ray and optical results.

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