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Citation: *The Journal of Chemical Physics* **84**, 5769 (1986); doi: 10.1063/1.449885

View online: <http://dx.doi.org/10.1063/1.449885>

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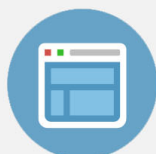
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X-ray diffraction investigation of Co(II) ions in borosilicate glasses

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(Received 7 October 1985; accepted 3 February 1986)

The radial distribution functions of cobalt glasses with 6%, 8%, and 14% CoO are compared with those of suitable cobalt-free borosilicate matrices leading to "difference distribution curves" representative of the cobalt structural arrangement. Analysis of the curves indicates that cobalt ions are surrounded by approximately four oxygen neighbors at the distance expected for fourfold coordination.

I. INTRODUCTION

Chemical and physical properties of metal ions incorporated in multicomponent glasses have been thoroughly investigated by optical methods,¹ and, more recently, by Raman, EPR, and Mössbauer spectroscopy.^{2,3} These techniques lead often to ambiguous results and moreover do not carry any information on structural details like bond lengths and coordination numbers of the ions. X-ray diffraction⁴⁻⁹ and EXAFS spectroscopy^{10,11} have been applied only sporadically in this field. We have therefore undertaken a systematic study on the structure of cations incorporated into glasses mainly using WAXS^{8,9} (wide angle x-ray scattering) and, whenever possible, EXAFS¹¹ and SAXS¹² (small angle x-ray scattering).

Radial distribution functions (WAXS data) have been interpreted by the method of difference curves. Structural arrangement of sodium ions in borate glasses has been inferred by comparison of their radial distribution functions with those from glasses where sodium was replaced by the same molar amount of lithium.⁸ Likewise, iron coordination and Fe-O distances in several iron(III) borosilicate glasses have been obtained by comparison of their radial distribution functions with that of iron-free glass matrix⁹ and confirmed by EXAFS analysis of the same samples.¹¹

We report herewith the results obtained by application of this method to Co-containing glasses. The characteristic deep blue color of these materials is due to a distorted fourfold oxygen coordination of cobalt ions, which produces a typical triplet at 600 nm.¹³ Sixfold coordination, which has been observed in borate glasses of very low alkali content, results in a pale pink color, and therefore in a different spectrum. However, according to Wong and Angell,² "the analysis of Co(II) spectra is complicated somewhat by the fact that, when the ligands coordinated in the two symmetries are chemically the same, both octahedral and tetrahedral spectra fall in the same frequency region." Furthermore, the optical extinction coefficient of sixfold coordinated Co(II) is smaller than the fourfold one and it could happen that the optical absorption bands of sixfold coordinated Co(II) are hidden by the fourfold coordinated Co(II) ones. Therefore,

no conclusive structural information has been obtained on these glasses up to now.

II. EXPERIMENTAL

Two sets of samples (Tables I and II) were prepared by weighted amounts of reagent grade SiO₂, B₂O₃, and Na₂CO₃ (Carlo Erba), using different matrix composition and experimental procedure; this was rigorously held fixed within each set. Reagents were ground in an agate ball mill. For the set *M*, a batch of powder was fused for 1 h at 1573 K and the melt was cast in cold water, dried, and ground to obtain a glass frit. The frit was then melted (with or without the appropriate amount of "black cobalt oxide," Carlo Erba reagent grade) for 2 h at 1573 K and 45 min at 1673 K, then cast in an aluminum mold and annealed for 30 min at 823 K.

For *M'*, the powders were melted in a covered platinum crucible for 3 h at 1773 K under normal atmosphere. The melt was then cast in an aluminum mold of suitable shape and annealed at 873 K for 15 min.

The samples were analyzed by standard methods for B, Na, and Co to 1% accuracy and Si determined by difference. Density was determined by an electronic Westphal balance using water as a reference liquid. Analytical data are reported in Tables I and II; in *M* samples composition did not change during preparation, while a loss of B₂O₃ and Na₂O was observed in *M'* ones. For this reason some stoichiometric coefficients in Table II are not identical in the glass and in the matrix.

The θ - θ x-ray diffractometer and the procedure for data normalization have been described elsewhere.¹⁴⁻¹⁶ Data from 1° to 70° θ , corresponding to ($s = 4\pi \sin \theta / \lambda$) from 0.3 up to 16.6 Å⁻¹ were collected with Mo $K\alpha$ radiation. At least 100 000 counts were collected at each preset discrete point. The observed intensity were corrected for background, absorption, polarization, and normalized by a semiempirical method.¹⁷ The structure functions $i(s)$ (Fig. 1) were obtained according to

$$i(s) = I_{e.u.} - \sum n_i f_i^2(s), \quad (1)$$

where $I_{e.u.}$ 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 according to

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TABLE I. Density and composition (in wt.%) of the glasses investigated. Extended and short reference names, used in the text, are given in column 1.

Glass	d (g cm ⁻³)	SiO ₂	B ₂ O ₃	Na ₂ O	CoO
SIBNA (<i>M</i>)	2.283	57.10	33.08	9.82	...
SIBNACO6 (Co6)	2.390	53.67	31.10	9.23	6.00
SIBNA2 (<i>M'</i>)	2.522	57.88	21.77	20.35	...
SIBNA2CO8 (Co8)	2.584	55.44	18.58	17.86	8.12
SIBNA2CO14 (Co14)	2.659	50.62	18.16	17.32	13.90

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

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

$$\{[\sum n_i f_i(0)]^2 / [\sum n_i f_i(s)]^2\} \exp(-ks^2)$$

with $K = 0.005$. Figure 2 shows the distribution curves in the differential form, $D(r) - 4\pi r^2 \rho_0$, up to 12 Å. Figure 3 shows the $D(r)$ functions of the cobalt glasses compared to those of the respective matrices.

III. ANALYSIS OF RESULTS

A. Inspection of radial curves

The radial curves, reported in Figs. 2 and 3, show similar shapes, which reflect the predominance of the matrix with respect to the incorporated cation. Apart from the ripples in the 0–1.2 Å region, which have no physical meaning, the main peaks are easily attributed to specific interactions. The peak at 1.6 Å is mainly due to Si–O interactions and, to a minor extent, to B–O interactions which fall between 1.37 and 1.53 Å depending on alkali content.^{3,18} The peak at 2.55 Å results from O–O interactions within SiO₄, BO₃, and BO₄ units, and from Na–O interactions expected at 2.35–2.40 Å^{8,19} and the peak at 3.1 Å is mainly due to Si–Si interactions.^{20,21}

The significant characteristics are: (i) the general shape of the matrix radial curve is not greatly affected by the addition of cobalt cations, indicating that the structure of the matrix remains substantially unaltered when the cobalt is present; (ii) the left sides of the dominant peak at 1.6 Å are coincident in each glass series, indicating that the nearest coordinations in the matrix network are unchanged; (iii) the right sides, on the other hand, become higher and the peak

area increases with the metal content. This happens just in the region around 2 Å, where Co–O interactions are expected to occur.

B. Difference curve analysis

The total radial function $D(r)$ obtained according to Eq. (2) is a sum of partial functions $D_{ij}(r)$ relative to each atom pair $i-j$:

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

where the summations are taken over the composition unit to which the intensities are normalized.

Let us now consider two samples, a glassy matrix (M) and a glass (G) obtained by introducing some x -type atoms in M . Their composition units can be chosen so that $n_i^G = n_i^M$ if $i \neq x$. If we can assume that the presence of guest atoms in the glass G produces no perturbation in the preexistent network, then $D_{ij}^G(r) = D_{ij}^M(r)$, ($i, j \neq x$) and

$$\Delta D(r) = D^G(r) - D^M(r) = n_x \sum_j (2 - \delta_{xj}) D_{xj}(r), \quad (4)$$

where δ is the Kronecker function. The difference of the experimental radial curves is then representative of the short range order around the x atom only.

However, some (or all) n_i may be different (e.g., due to the preparation); in this case the $\Delta D(r)$ curve is approximately described by

$$\Delta D(r) = n_x \sum_j (2 - \delta_{xj}) D_{xj}(r) + \sum_{i \neq x} \Delta n_i \sum_{j \neq x} D_{ij}(r). \quad (5)$$

Figure 4 shows the difference curves obtained from the $D(r)$ functions given in Fig. 3. Co–O peaks centered at 2.04 and 1.98 Å for M and M' glasses, respectively, are clearly evident. A second peak, falling around 3.15–3.20 Å in all glasses, is indicative of the “second sphere” interactions

TABLE II. Concentrations (in molarity) and atomic ratios (n_i) of the glasses elements. V_{Si} are the stoichiometric volumes used for data normalization and μ the absorption coefficient. The two last columns give the boron and the sodium composition differences (Δn_i) of each glass with respect to the matrix.

Glass		Si	B	Na	O	Co	V_{Si} (Å ³)	μ (cm ⁻¹)	Δn_B	Δn_{Na}
<i>M</i>	mol/ℓ	21.70	21.70	7.23	79.56	...	76.522	6.66		
	n_i	1.000	1.000	0.33	3.66	...				
Co6	mol/ℓ	21.35	21.35	7.12	80.20	1.91	77.777	11.29		
	n_i	1.000	1.000	0.33	3.75	0.090				
<i>M'</i>	mol/ℓ	24.30	15.77	16.57	80.52	...	68.338	7.98		
	n_i	1.000	0.649	0.682	3.314	...				
Co8	mol/ℓ	23.84	13.79	14.89	78.62	2.80	69.659	14.69		
	n_i	1.000	0.579	0.625	3.298	0.118			-0.070	-0.057
Co14	mol/ℓ	22.40	13.87	14.86	77.98	4.93	74.132	18.81		
	n_i	1.000	0.663	0.619	3.481	0.220			-0.030	-0.019

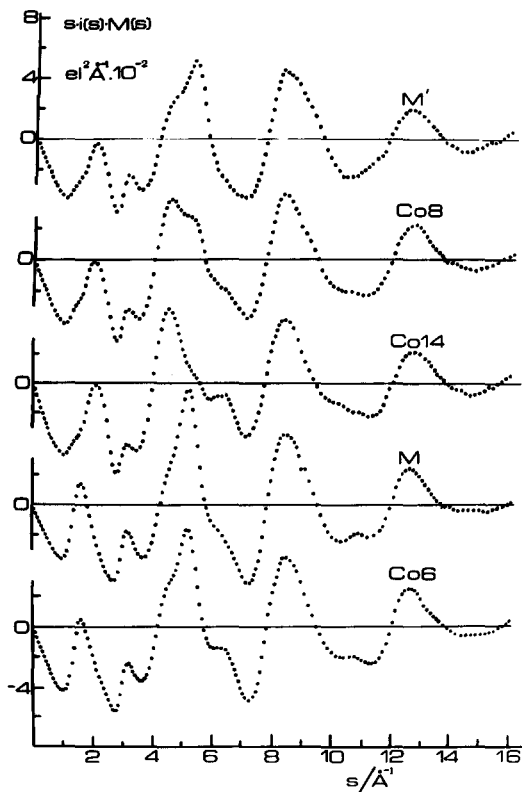


FIG. 1. Experimental reduced intensity functions, $s.i(s).M(s)$, for matrices (M and M') and for cobalt glasses (Co8, Co14, and Co6).

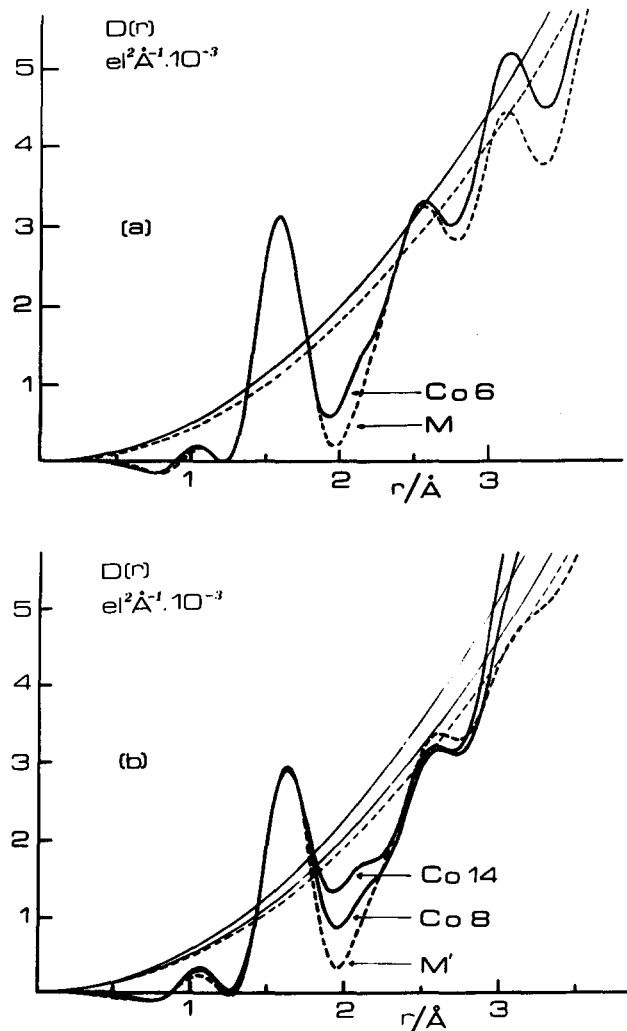


FIG. 3. (a) and (b) Radial distribution functions, $D(r)$, of cobalt glasses (solid lines) compared to the $D(r)$ functions of the matrix (dotted lines) for M and M' series, respectively. In all cases the radial curves have been normalized to a unit of volume containing one silicon atom (V_{Si} in Table II).

between metal and silicon and/or boron. The negative region at 2.5 Å in Co8 and Co14 essentially reflects the compositional difference in boron and sodium (see Δn_{Na} and Δn_B in Table II).

The quantitative analysis through Eq. (5) was then carried out; theoretical peaks were calculated by Fourier transforming the pair contributions to the structure functions defined as

$$(2 - \delta_{pq}) n_p f_p f_q \frac{\sin sr_{pq}}{sr_{pq}} e^{-b_{pq}s^2}, \quad (6)$$

where r_{pq} is the average distance between atoms p and q , and b_{pq} the associated Debye-Waller factor. The sum of these peaks, $\Delta D(r)_{calc}$, inclusive of second sphere interactions around metal ions as well as corrections resulting from the composition difference in both Na and B, was then matched to the experimental curve. The structural parameters for Na and B interactions were taken from the literature.^{3,8,18,19}

The fitting was performed through a computer video-graphic system which allowed continuous parameter adjust-

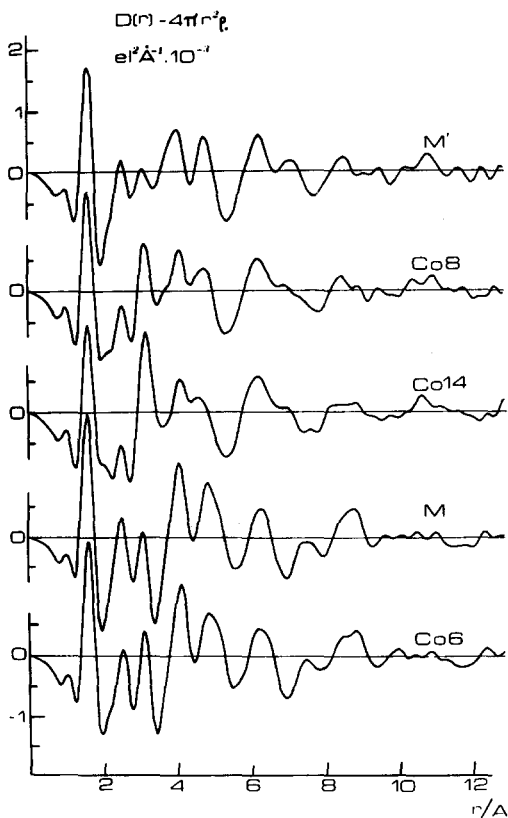


FIG. 2. Radial distribution functions in the differential form, $D(r) - 4\pi r^2 \rho_0$, for the five glasses investigated, are shown in the 0-12 Å range.

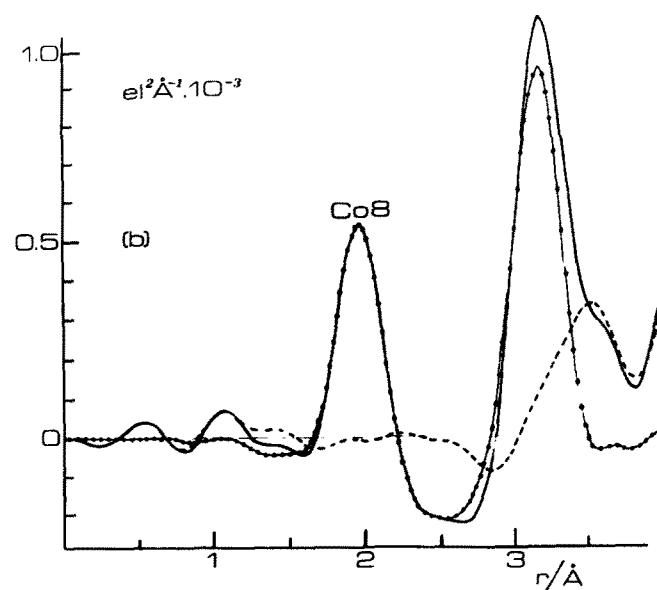
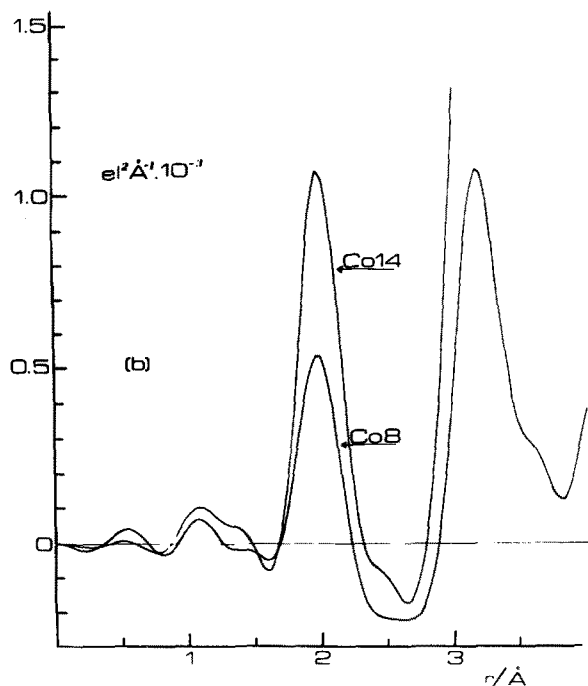
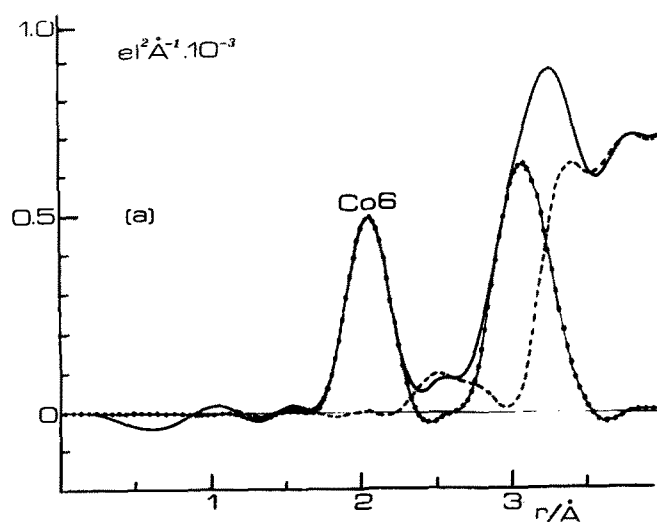
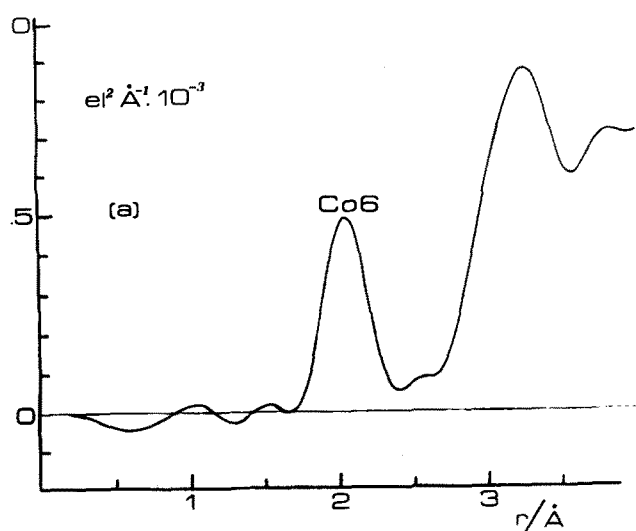


FIG. 4. Radial distribution difference curves, $\Delta D(r)_{\text{exp}}$ [see Eq. (5)] for the Co6 (a) and the Co8 and Co14 (b) glasses. With respect to Fig. 3 the y scale of this figure is enlarged five times.

ments until a satisfactory match of calculated and experimental functions was achieved. In practice this means that, once contiguous interactions were properly fixed, Co-O parameters ($r_{\text{Co-O}}$, $b_{\text{Co-O}}$, $N_{\text{Co-O}}$) were adjusted so that the calculated sum of peaks reproduced the Co-O experimental peak, leaving out a smoothed difference,

TABLE III. Structural parameters (r , b , N = distance, temperature factor, and neighbor number) obtained for Co(II) first coordination sphere.

Glass	$r_{\text{Co-O}}$ (Å)	$b_{\text{Co-O}}$ (Å ²)	$N_{\text{Co-O}}$
Co6	2.04	0.0049	3.95
Co8	1.97	0.0047	3.60
Co14	1.98	0.0041	3.55

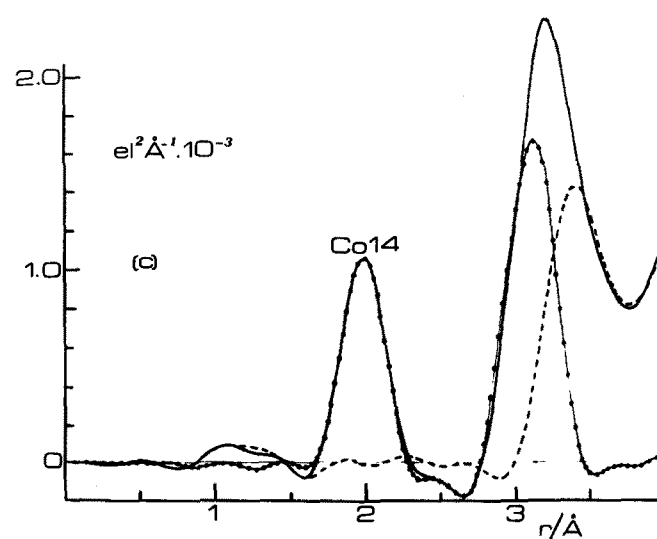


FIG. 5. Curve fitting of the Co-O peaks for Co6 (a), Co8 (b), and Co14 (c) glasses. The sum of the calculated peak shapes $\Delta D(r)_{\text{calc}}$ is shown by solid lines and dots, and has been drawn by using the parameters of Tables III and IV. The dashed lines are the difference $\Delta D(r)_{\text{exp}} - \Delta D(r)_{\text{calc}}$ and show no unresolved significant peaks up to ~ 3 Å. Notice change of scale in (c).

TABLE IV. Structural parameters (r , b , N = distance, temperature factor, and neighbor number) introduced to account for metal second-shell interactions. The parameters used for correction of composition difference in boron and sodium are also reported.

Glass	B-O			(O-O) _{BO_x}			Na-O			Me-2nd		
	r	b	N	r	b	N	r	b	N	r	b	N
Co6										3.06	0.009	2.5 (Co-Si)
										2.78	0.014	1.5 (Co-B)
Co8	1.46	0.002	4	2.47	0.005	6	2.35	0.03	6	3.15	0.007	2.25 (Co-Si)
										3.09	0.007	1.35 (Co-B)
Co14	1.46	0.002	4	2.47	0.005	6	2.35	0.03	6	3.10	0.007	2.22 (Co-Si)
										3.00	0.007	1.33 (Co-B)

$\Delta D(r)_{\text{exp}} - \Delta D(r)_{\text{calc}}$, lying approximately on the zero line. The final fits for the three glasses are shown in Fig. 5. Tables III and IV give the structural parameters used. All calculations were performed using a modified version of the KURVLR program.²²

IV. DISCUSSION

The difference curve method has been already applied to glasses at a qualitative level.^{7,23,24} A quantitative analysis can be carried out through Eqs. (3)–(5) and it will be valid as far as atomic interactions in the matrix are not substantially altered by the presence of the cation. Rigorously it is unlikely that this condition is satisfied. However, if we limit the analysis to the first coordination shell of the cation, $r < 2.5$ Å, it is sufficient that the hypothesis holds within this distance range. Since this range comprises contributions from the rigid units (SiO₄, BO₃, and BO₄) of the glassy network, the assumption is likely to be realistic. An experimental support is given by the left side shape and the maximum position of the main peak in the radial curves (Fig. 3), which stay unaltered within each glass series when cobalt ions are present.

The method is strictly dependent on the utmost care in experimental procedure; the metal ion contribution to the total scattered intensity from the sample is relatively low, as Fig. 1 shows. To evaluate this contribution by means of the difference method, the preparation procedure, the set up of the x-ray apparatus, the counting statistic, and the treatment of experimental data must be kept rigorously constant within each set of samples. Figures 3 and 4 show that troubles coming from systematic errors have been really minimized. In fact, spurious ripples in Fig. 3 are small and, moreover, very similar in the various cases. As a consequence, only ripples much smaller than the real peaks remain at low r in the difference curves of Fig. 4.

Though the cobalt oxide used in the preparation is a mixture of cobalt oxides, the conditions of preparation assure that Co(III) ions are totally unstable,² so that, at the end of the preparation, all the cobalt is present as Co(II). The Co–O bond length in octahedral configuration is ~ 2.13 Å.²⁵ In Co₃O₄, distances of 1.95²⁶ and 1.99 Å²⁷ for Co(II)–O in tetrahedral configuration are reported. Thus, the distance parameters, together with the coordination numbers, strongly suggest fourfold cobalt coordination.

In order to account for the compositional differences between glasses and matrix in the M' series, the analysis of the first peak was done by considering also the second term

in Eq. (5). Sodium and boron interactions, falling on the left and right sides of the Co–O peak, can influence the Co–O structural parameters. The influence was evaluated by performing several preliminary fits and allowing some variance of B and Na coordination (within plausible physical values^{3,8,18,19}) and of their concentrations (within the analytical uncertainty). We realized that coordination numbers have an uncertainty of about 0.2–0.3 oxygen neighbors for the M' glass series. The uncertainty for Co6 sample is even lower. The $r_{\text{Co-O}}$ distances, on the other hand, are nearly unaffected by the other parameters given in Table IV and by variation in concentrations, and have a reliability of approximately 0.01–0.02 Å.

Obviously, these are only part of the total uncertainty of the parameters, since imprecisions could also arise from statistical errors in the measurements, from other systematic errors and, above all, from the partial validity of the assumptions of the method. An evaluation of these imprecisions is clearly very difficult or impossible at all. Only further applications of the method and comparison of the results with the information from other sources will give a definite answer to this point. Accordingly, we may propose the empirical criterion of using the discrepancy between WAXS⁹ and EXAFS¹¹ determinations of Fe(III) coordination in similar glasses as an evaluation of the reliability limits of the parameters. Thus we can conclude that the differences in the distances and coordination numbers given in Table III are not significant.

One more thing can be deduced from the difference curves. Similarly to what was found for iron(III),⁹ they all show sharpened shapes in both first and second main peaks, which represent first and second coordination shells around the metal ion. This means that the metal ions occupy well defined positions in the total amorphous network. The Co-coordinated oxygen atoms are probably bonded to external silicon and boron atoms, leading to easily detectable metal–boron and metal–silicon interactions. In Fig. 5 it can be seen that a very simple model (see parameters in Table IV) can account for most of the area beneath the second peak. Of course, as far as the information beyond the first coordination shell is concerned, the present results are just the starting point for further investigations.

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