EXAFS studies of cobalt oxides and oxide glasses†

R PARTHASARATHY, RAVI V PRASAD⁺, P R SARODE and
K J RAO*

Solid State and Structural Chemistry Unit, Indian Institute of Science,
Bangalore 560012, India

MS received 31 December 1981

Abstract. The EXAFS of Co^{2+} has been studied in rare earth cobaltites and in sulphate and borate glasses. It has been found that the environment of Co^{2+} ions is very similar in these cases. It appears feasible to study local structures in glasses using probe ion EXAFS.

Keywords. EXAFS; ionic glasses; crystals.

1. Introduction

Rare earth cobaltites have been well investigated in recent years and their structures are known in sufficient detail (Raccah and Goodenough 1967 ; Demazeau *et al* 1974). An EXAFS study of such model compounds would be expected to furnish information (*e.g.*, phase-shifts) which could then be used in EXAFS analysis of glasses containing cobalt. Considering thecomparative paucity of EXAFS data on crystalline compounds whose structure is known in detail, we felt that an EXAFS study of these compounds could also provide much insight on the scope of the technique itself.

In this paper we report results of EXAFS investigations of crystalline $LnCoO_3$ (where Ln = La, Nd, Dy and Yb) compounds and of some cobalt-containing glasses belonging to the systems Na_2SO_4–K_2SO_4–$ZnSO_4$–$CoSO_4$ and CoO–B_2O_3. The ternary sulphate system Na_2SO_4–K_2SO_4–$ZnSO_4$ has been extensively studied in this laboratory (Sundar and Rao 1980 ; Sundar and Rao 1981). At low concentrations, the isovalent Co^{2+} ions are known to enter Zn^{2+} sites due to similarity of sizes (Sundar and Rao 1981). At higher concentrations, however, the site symmetry of the Co^{2+} ion is not known. A Co K-edge EXAFS study might be expected to yield valuable information on both concentration regimes.

P.(A)—3

2. Experimental

The preparation of the rare earth cobaltites from the cobalticyanide (Demazeau *et al* 1974) and of sulphate glasses from component sulphates (Sundar and Rao 1980) have both been reported earlier. Glasses with higher cobalt content were progressively more unstable with respect to devitrification. The Co-borate glass was prepared by melting together $CoSO_4$ and H_3BO_3 in a graphite crucible.

Co K-absorption edge EXAFS was measured using a bent crystal spectrograph and a Carl-Zeiss microdensitometer as described previously (Parthasarathy *et al* 1981). Data were available upto about 400 eV beyond the edge. Details with regard to the procedure for data analysis and Fourier transformation along with subsequent curve-fitting procedures have been described elsewhere (Cramer 1978 ; Parthasarathy *et al* 1982).

3. Results and discussion

Figure 1 shows the radial structure functions (RSF's) obtained for the crystalline compounds. Figure 2 shows the RSF's obtained for the glasses. Distances corrected for phase-shifts are listed in table 1.

3·1. *Cobalt in rare earth cobaltites LnCoO₃*

Rare earth cobaltites are known to crystallise in the perovskite structure (Demazeau *et al* 1974). The first peak in the RSF at 1.92 ± 0.03 Å may be identified as the

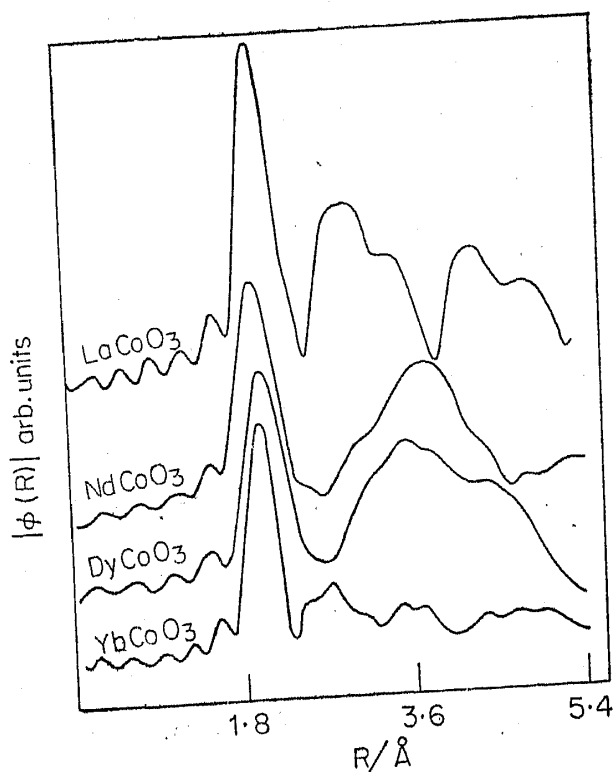**Figure 1.** RSF's of the crystalline cobaltites.

Table 1. Phase shifts and distances from RSF's of cobalt oxides and oxide glasses.

No.	Compounds	a^* (Å)	Distances (Å)					
1.	LaCoO₃	0·034	1·91	2·05	2·91	3·35	4·25	4·71
2.	NdCoO₃	0·046	1·92		2·85	3·29	3·83	4·37
3.	DyCoO₃	0·020	1·96		2·83	3·26	3·80	4·34
4.	YbCoO₃	0·04	1·91	2·38	2·67	2·95	3·35	3·60
5.	Sulphate Glass 1	0·081	2·02			3·42	4·61	5·73
6.	Sulphate Glass 2	0·029	1·98			3·71	4·53	5·43
7.	Sulphate Glass 3	0·073	2·02			3·31	3·85	4·57
8.	Borate Glass	0·065	1·90			3·49	4·64	5·76

Co–O distance. This distance is almost independent of the rare earth ion. Phase corrections were made using YbCoO₃ as a standard (Cramer 1978). For peaks other than the first, we felt that use of the curve fitting procedure was inadvisable since their amplitudes in the RSF were low. Phase corrections, a^*, were calculated using the expression,

$$a^* = R_{\text{standard}} - R_{\text{Fourier transform}}.$$

$|a^*|$ was then added to the appropriate peak in the RSF's of the other cobaltites. The feature at 2·9 Å, however, is rather perplexing and we are unable to ascertain its origin from available crystal data.

3·2. Cobalt in glasses

3·2a *Sulphate glasses* : The similarity of the RSF's of these glasses to those of the crystalline cobaltites suggests that the co-ordination of Co²⁺ in these are similar. This is quite in keeping with the structural model proposed earlier for these glasses (Sundar and Rao 1980). On the basis of this model, we assign the peak at 1·90 Å to the Co–O distance. Similarly, the 3·7 Å peak may be assigned to the Co–K separation ; the peak at 5·5 Å could possibly describe the Co–Co or Co–Zn distances.

At low Co²⁺ concentration, the sites that Co²⁺ ions may occupy are limited to those of Zn²⁺ ions in the glass. With these concentrations, one would expect site distortions and the asymmetric first peak does in fact reflect the existence of a range of distortions. Increasing the Co²⁺ concentration would result in the formation of a distinct but similar type of Co²⁺ site in the glass and the formation of characteristic Co²⁺ sites is apparent in the *symmetric* nearest neighbour peak in figure 2. Glasses 2 and 3 (see figure 2) show a sudden decrease in RSF amplitude at distances > 4Å. Such decreases in RSF amplitude beyond distances ~ 2R (where R is the radius of the structural unit) are reminiscent of the EXAFS
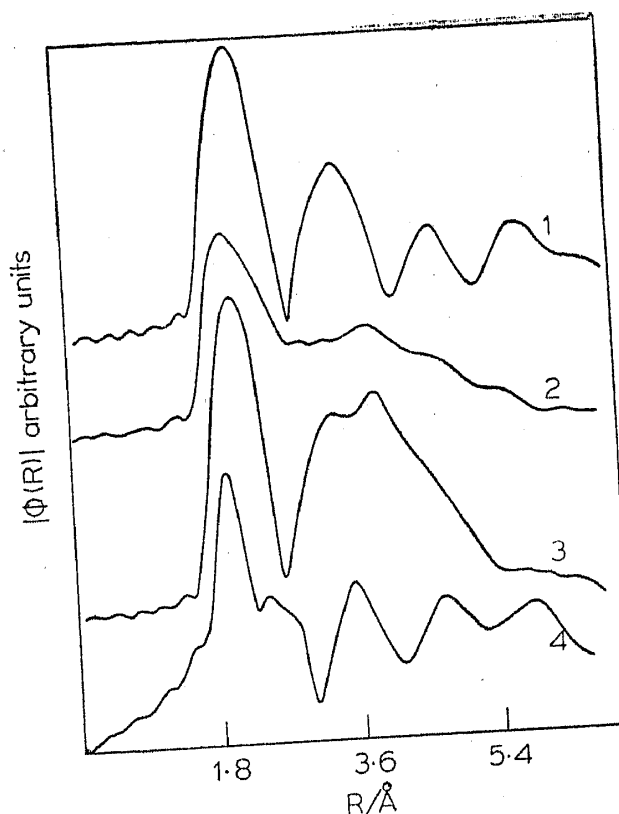
Figure 2. RSF's of cobalt oxide glasses. The numbers indicate the following molar compositions (1) $ZnSO_4 : Na_2SO_4 : K_2SO_4 : CoSO_4 : : 15 : 30 : 30 : 25$ (2) $25 : 25 : 25 : 25$, (3) $20 : 20 : 20 : 40$ and (4) $CoO : B_2O_3 : : 20 : 80$.

of metallic glasses where dense random-close-packing models are valid (Wong 1980). In glass 1, however, the decrease in RSF amplitude for $R > 4Å$ is not so significant and peaks are discernible to $5 \cdot 5Å$. It may be recalled that these distances in glass 1 are attributed to Co–Zn or to Co–Co. The decreased structure in the RSF due to increasing Co^{2+} concentration, allows for two possible explanations. One is that the scattering amplitude of Co^{2+} ions is predominant and that scatterers further away than the " line-of-sight " Co^{2+} scatterers are consequently screened. The RSF in this case will then show only the presence of atoms in between the absorber Co^{2+} and the " line-of-sight " Co^{2+} scatterer. The other explanation could be that the formation of typical Co^{2+} sites in glasses containing higher concentrations of Co^{2+} gives rise to an intrinsically less structured RSF and this may obscure features due to Co^{2+} in Zn^{2+} sites typical of dilute glasses.

3·2b. *Borate glass* The noise level in the EXAFS of the borate glass is considerably high (note the high background level in the RSF for $R < 1 \cdot 5Å$). The nearest neighbour peak at $1 \cdot 90$ Å (the Co–O distance) (which was merely asymmetric in the sulphate glasses) is now resolved into two distinct components. The sharpness of the first peak at the normal Co–O distance, indicates the presence of a single structural unit. The peak at $2 \cdot 70$ Å has a rather large width and indicates random orientation of this structural unit about the Co^{2+} ion. The other distances in the RSF are largely similar to those of the sulphate glasses and suggest octahedral co-ordination of Co^{2+} by BO_4^- ions.

4. Conclusion

In brief, the Co^{2+} site symmetry in ionic and in covalent glasses appears to be very similar to that in the rare earth cobaltites. This rather interesting feature may ensure from the characteristic O^{2-} ligancy of the Co^{2+} ions. Further, structural information from EXAFS (related to the structuredness of the RSF) appears to be reduced in the presence of a higher concentration of scatterers. The origin of this effect is, however, not known.

Acknowledgements

References

Cramer S P 1978 SSRL *Report* 78/01 Stanford Synchrotron Research Laboratory (Stanford USA)

Demazeau G, Pouchard M and Hagenmuller P 1974 *J. Solid State Chem.* 9 202

Parthasarathy R, Sarode P R and Rao K J 1981 *J. Mat. Sci.* 16 3222

Parthasarathy R, Rao K J and Rao C N R 1982 *J. Phys. C: Solid State Phys.*, 15 3649 (communicated)

Raccah P M and Goodenough J B 1967 *Phys. Rev.* 155 932

Sundar H G K and Rao K J 1980 *J. Chem. Soc. Faraday Trans. I* 76 1617

Sundar H G K and Rao K J 1981 *J. Non-Cryst. Solids.* (communicated)

Wong J 1980 in *Topics in Applied Physics*, Vol. 46 *Metallic Glasses*, (eds) H J Guntherodt and H Beck Chapter 4 (Berlin : Springer-Verlag)