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Electron spin resonance in phosphate glasses containing mixed transition metal ions

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Phosphate glasses containing mixed Cu^{2+}/Ni^{2+} and Cu^{2+}/Co^{2+} oxides have been examined. A pronounced decrease in the optical absorption at 830 nm due to the Cu^{2+} ions is observed as the CuO in the glasses is gradually replaced by NiO or CoO and the decrease is accompanied by a pronounced decrease in the strength of the electron spin resonance (ESR) signal at 9.52 GHz. By combining the ESR and optical absorption data it is concluded that the decrease in concentration of Cu^{2+} ions in phosphate glasses may be due to an oxidation–reduction mechanism between two valency states of the two different transition metals, of the form $Cu^{2+} + Ni^{+} \rightarrow Cu^{+} + Ni^{2+}$ and $Cu^{2+} + Co^{+} \rightarrow Cu^{+} + Co^{2+}$.

1. Introduction

Electron spin resonance (ESR) spectroscopy is particularly concerned with the investigation of paramagnetic centres which may be produced by such processes as radiation damage (X-rays, γ-rays etc.) and by the incorporation of transition metal ions into the system.

One of the first detailed investigations of glassy materials incorporating transition metal ions was undertaken by Sands [1] on the soda-lime–silicate glass-based system. Landsberger and Bray [2] utilized the ESR technique for determining the ratio of $[V^{4+}]/[V^{5+}]$ in phosphorus pentoxide and vanadium pentoxide glasses, and the electronic conductivity of semiconducting phosphate glasses containing a transition metal in two different oxidation states has been further studied by Nester and Kingery [3], Hansen [4], Joffe *et al.* [5], Linsley *et al.* [6] and by Moridi and Hogarth [7] who all found charge transfer by electron hopping from a lower to a higher valency state. Less work has been reported in glasses containing two different transition metal oxides. Bogomolova *et al.* [8, 9] studied vanadium phosphate glasses doped with copper oxide and also investigated the effect of Co^{2+} on the ESR spectra of Cu^{2+}, V^{4+}, Mn^{2+} and W^{5+} ions in different glassy media, explaining the results in terms of cross-relaxation processes between the two spin systems and also by spin diffusion. For a barium phosphate glass containing V_2O_5 and CoO, Bogomolova *et al.* [10] explained the decrease in the V^{4+} ESR signal by spin diffusion and with V_2O_5 and CuO invoked a chemical exchange mechanism of the form

$$V^{4+} + Cu^{+} \rightarrow V^{5+} + Cu^{+}.$$

More recently, Bandyopadhyay [11] studied the optical spectra of borate glasses containing the oxides of vanadium, iron and copper both separately and mixed. The ESR spectra of the latter showed complicated interaction patterns for two different transition metal ions where all four possible oxidation states exist for the mixed ions with a possible pairing of mixed ions in the form of oxygen-bridged associates (M^{x+}–O–N^{y+}) occurring.

The absorption spectra of transition metal ions in silicate glasses have been examined by Bates [12] and by Weyl [13], but work on phosphate glasses has been carried out by Haddon *et al.* [14] who found an absorption band at 852 nm (11 850 cm^{-1}) and attributed this to Cu^{2+} ions in an octahedral field with strong tetragonal distortion. The absorption bands at 536 nm (18 660 cm^{-1}), 586 nm (17 060 cm^{-1}) and 615 nm (16 260 cm^{-1}) are attributed to Co^{2+}. Weyl [13] attributes these bands to six-coordinated Co^{2+} ions. Haddon *et al.* [14] also attribute the absorption band at

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TABLE I Some parameters of copper phosphate glasses containing nickel

Number	Glass sample	P_2O_5 (mol %)	CuO (mol %)	NiO (mol %)	Total Cu in 100 g of glass	Cu^{2+} in 100 g of glass	Cu^+ in 100 g of glass	$C = \frac{[Cu^+]}{[Cu_{total}]}$
1	a	65	35	0	28	20.7	7.3	0.261
2	b	65	34	1	23.15	14.77	8.38	0.362
3	c	65	33	2	22.8	13.8	9	0.395
4	d	65	32	3	21.75	11.27	10.48	0.482
5	e	65	31	4	20.35	7.62	12.73	0.628
6	f	65	30	5	18.53	6.14	12.39	0.669
7	g	65	25	10	17.36	0.69	16.67	0.960
8	h	65	20	15	17.15	0.688	16.46	0.960
9	i	65	15	20	8.695	0.517	8.178	0.941

435 nm (23 300 cm^{-1}) to Ni^{2+} ions in phosphate glasses and suggest that the Ni^{2+} ion is octahedrally coordinated. A strong absorption band at 11 500 to 11 250 cm^{-1} has been also reported by Moridi and Hogarth [15] in copper–calcium–phosphate glasses as being due to Cu^{2+} in an octahedral environment with a strong tetragonal distortion.

In the present paper the results of ESR and optical absorption studies of $CuO–NiO–P_2O_5$ and $CuO–CoO–P_2O_5$ glasses are reported.

2. Experimental work

Copper–nickel–phosphate and copper–cobalt–phosphate glasses were prepared from analytical grade reagents CuO, NiO, CoO and P_2O_5. All glasses were prepared as 45 g samples in alumina crucibles. These were maintained at a temperature of 400° C for 1 h to minimize the tendency for P_2O_5 to evaporate and were then transferred to a second furnace for 3 h at 1100 to 1150° C in an air atmosphere. The melts were stirred from time to time to promote homogeneity and were then cast as disc-shaped glasses 1.5 to 2 cm diameter and about 2 to 2.5 mm thick. These discs were annealed at 400° C for 1 h. The compositions used cover the range 65% P_2O_5, $(35 - x)$% CuO and x% MO(M = nickel or cobalt) on a mole basis (see Tables I and II).

Electron spin resonance studies were carried out on the dry powdered glasses contained in a standard Varian 3 cm silica sample tube at room temperature and at X-band frequency using a Varian E.3 ESR spectrometer. For sample batches, all instrument settings were made at constant values, and gain settings were only varied as required. Copper sulphate was used as a standard for the spin concentration determination of Cu^{2+} in the glasses. Total copper in the glasses was determined by standard chemical procedures.

The optical spectra were measured using a Perkin–Elmer 402 spectrophotometer in the range 190 to 850 nm on films of thickness 20 to 30 μm. Samples were prepared by blowing thin films from the molten glass and the thicknesses were measured using a Sigma Comparator.

3. Experimental results

The ESR spectara of $CuO–P_2O_5$, $CuO–NiO–P_2O_5$ and $CuO–CoO–P_2O_5$ glasses are shown in Figs. 1 and 2, and with these glasses no copper hyperfine structure was discernible due to the high proportion of Cu^{2+} used. ESR spectra of transition

TABLE II Some parameters of copper phosphate glasses containing cobalt

Number	Glass sample	P_2O_5 (mol %)	CuO (mol %)	CoO (mol %)	Total Cu in 100 g of glass	Total Cu^{2+} in 100 g of glass	Cu^+ in 100 g of glass	$C = \frac{[Cu^+]}{[Cu_{total}]}$
1	Co(I)	65	34	1	23.84	16.53	7.31	0.307
2	Co(II)	65	33	2	23.1	15.28	7.82	0.339
3	Co(III)	65	32	3	22.19	11.39	10.80	0.387
4	Co(IV)	65	31	4	21.57	10.07	11.5	0.533
5	Co(V)	65	30	5	20.37	6.45	13.92	0.683
6	Co(X)	65	25	10	18.55	1.91	16.64	0.897
7	Co(XV)	65	20	15	15.24	0.4521	14.78	0.970
8	Co(XX)	65	15	20	7.3	0.2015	7.098	0.972

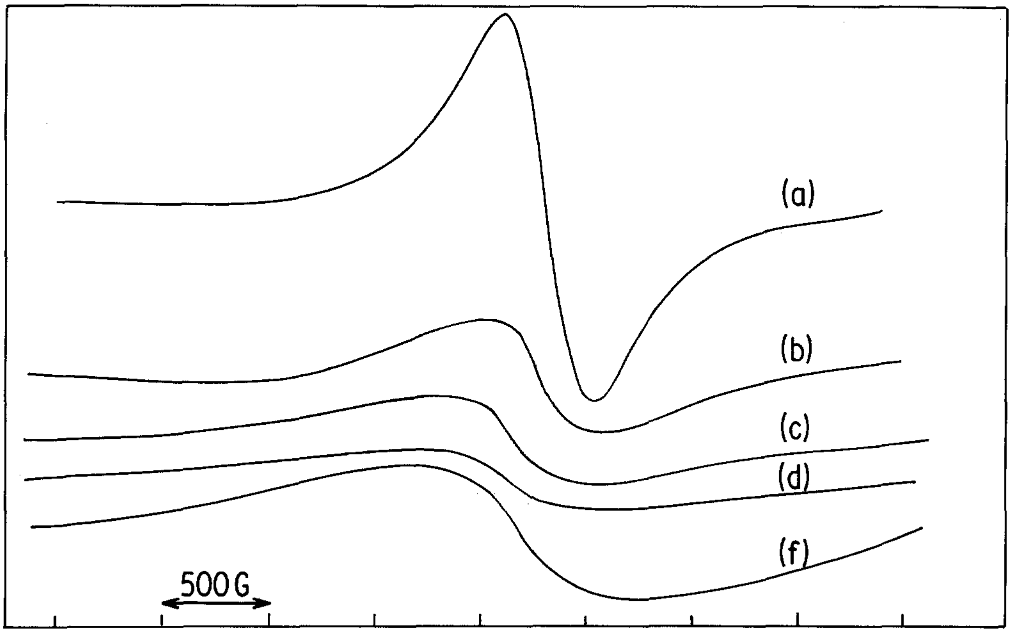

Figure 1 ESR spectra of some copper phosphate glasses containing nickel. (For curve f the system gain was increased.)

metal ions in phosphate glasses have been reported by Sayer and Mansingh [16]. Copper, vanadium and molybdenum gave strong signals, tungsten and iron weak signals and for cobalt and nickel no signals were observed. ESR spectra of copper–calcium–phosphate glasses have also been reported by Moridi and Hogarth [17].

In the case of NiO-doped glasses, even a 1% NiO level reduces considerably the otherwise strong copper signal and this continues to weaken and broaden as the NiO content is raised as shown by the plot in Fig. 3 where $C = [Cu^+]/[Cu_{total}]$ and where the concentration $[Cu^+]$ is estimated from the difference between total copper and the value

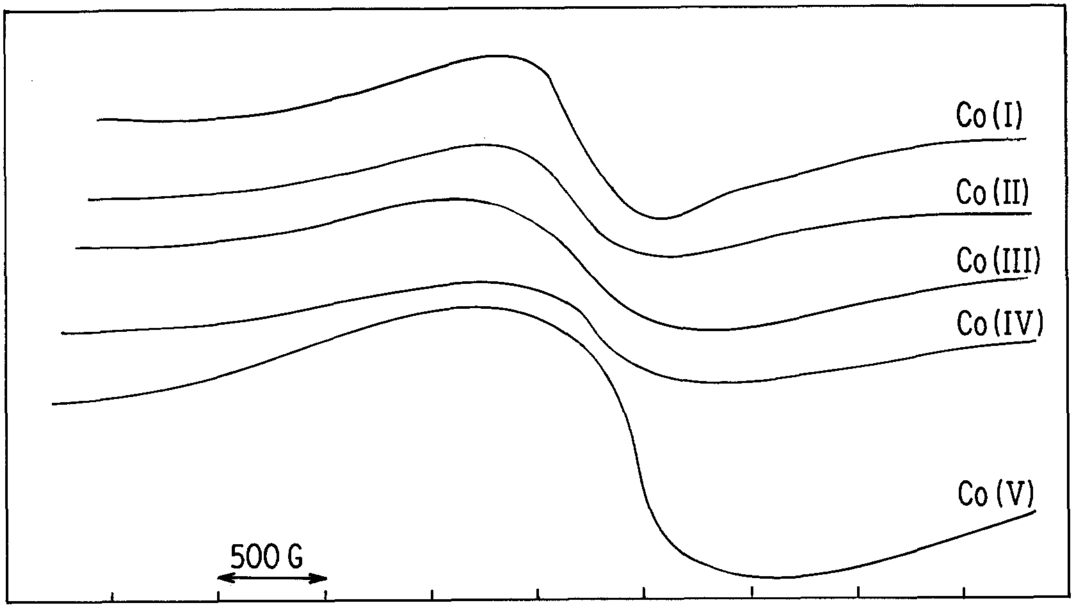

Figure 2 ESR spectra of some copper phosphate glasses containing cobalt. (Gain ranges are 4×10^4 for Co(I) and Co(II), 8×10^4 for Co(III) and Co(IV) and 2×10^5 for Co(V).)

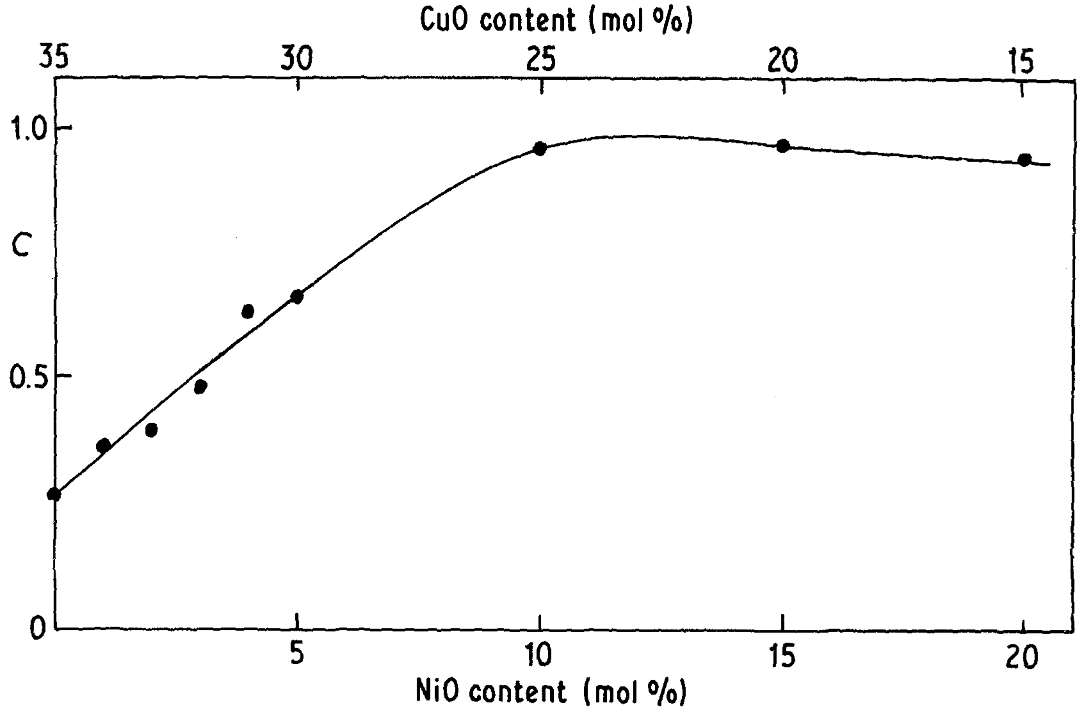

Figure 3 The variation of reduced valency constant *C* as a function of NiO and CuO contents.

of concentration $[Cu^{2+}]$ observed by ESR. The effect of added CoO on the copper signal is similarly recorded in Fig. 4. A graph plotted between $[Cu^{2+}]$ and the NiO content in mol% shows a gradual decrease of $[Cu^{2+}]$ with the increase of NiO up to 10% but after that the $[Cu^{2+}]$ remains very low indeed, as shown in Fig. 5. A similar graph (Fig. 6) shows the decrease of $[Cu^{2+}]$ with the increase of CoO.

The absorption spectra of CuO–P_2O_5, CuO–

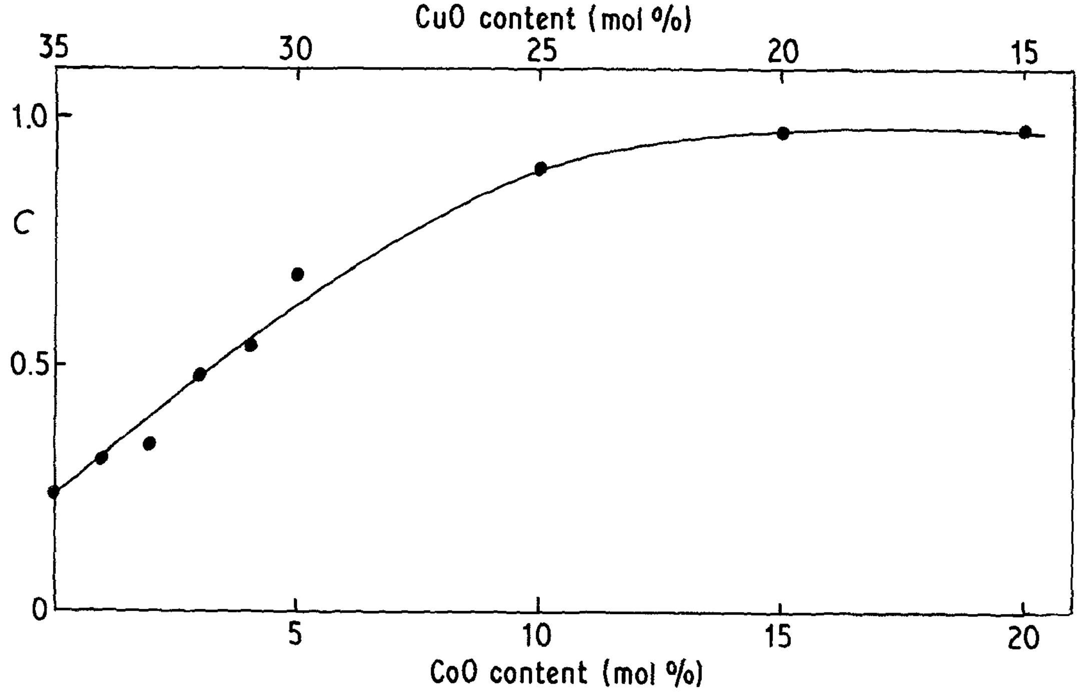

Figure 4 The variation of reduced valency constant *C* as a function of CoO and CuO contents.

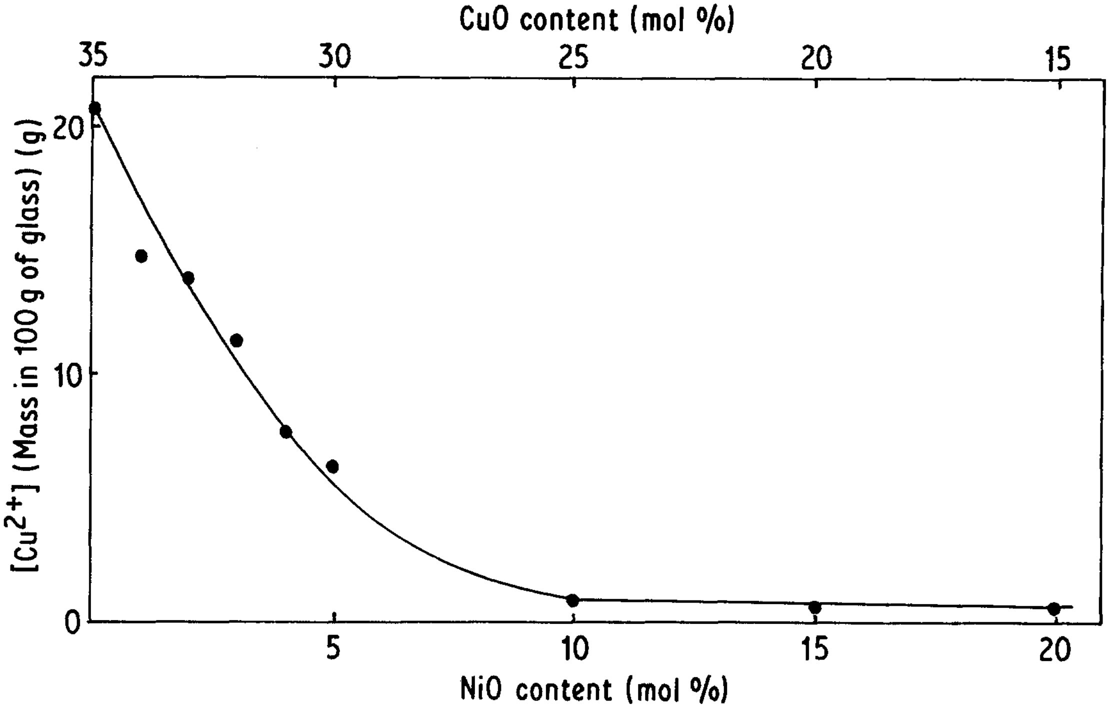

Figure 5 Decrease of concentration of Cu^{2+} ions derived from the ESR signal with decreasing CuO content and increasing CoO content.

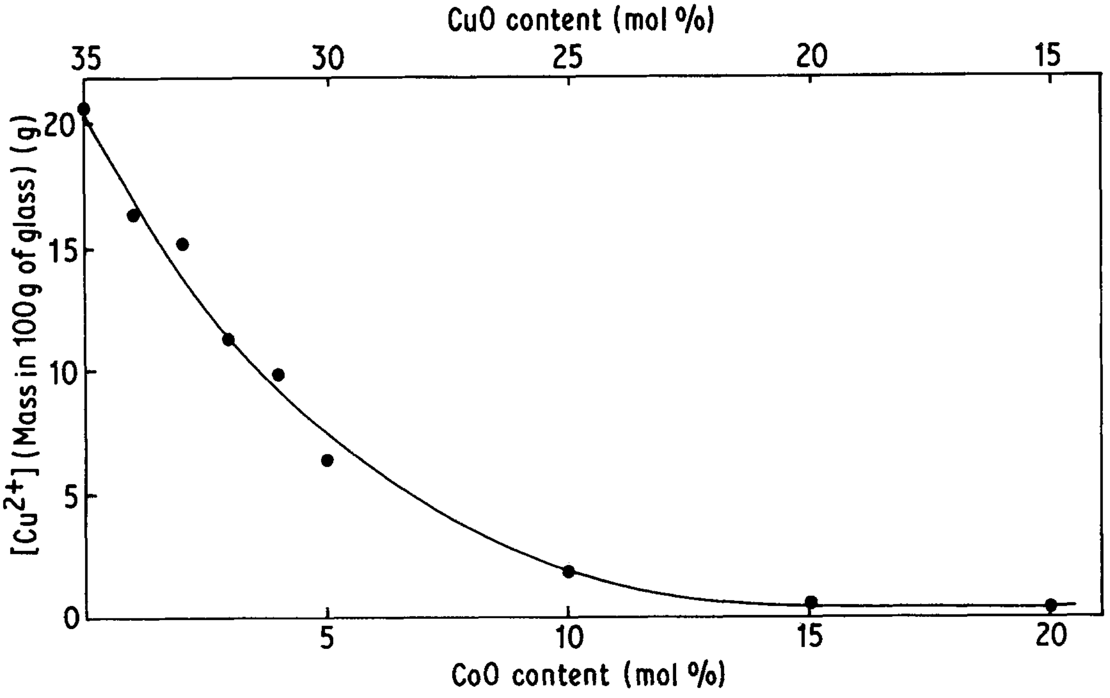

Figure 6 Decrease of concentration of Cu^{2+} ions derived from the ESR signal with decreasing CuO content and increasing NiO content.

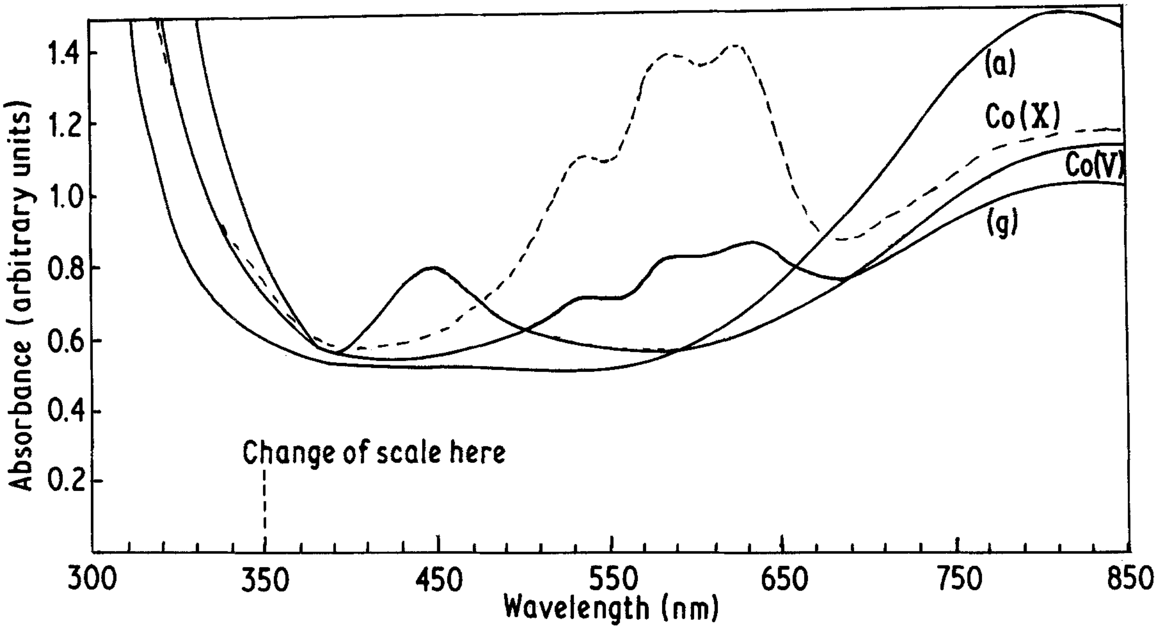

Figure 7 Optical absorption spectra of copper phosphate (a), copper–cobalt–phosphate (Co(X) and Co(V)) and copper–nickel–phosphate (g) glasses.

$NiO–P_2O_5$ and $CuO–CoO–P_2O_5$ glasses are shown in Fig. 7. An absorption band at around 440 nm and bands at 535, 590, 623 and 830 nm are observed. An absorption at 830 nm due to Cu^{2+} is observed for different compositions and there is a decrease in absorption as the concentration of NiO or CoO is increased. Figs. 8 and 9 are plots of absorption/thickness in μm as functions of NiO or CoO content and also show the decrease of $[Cu^{2+}]$.

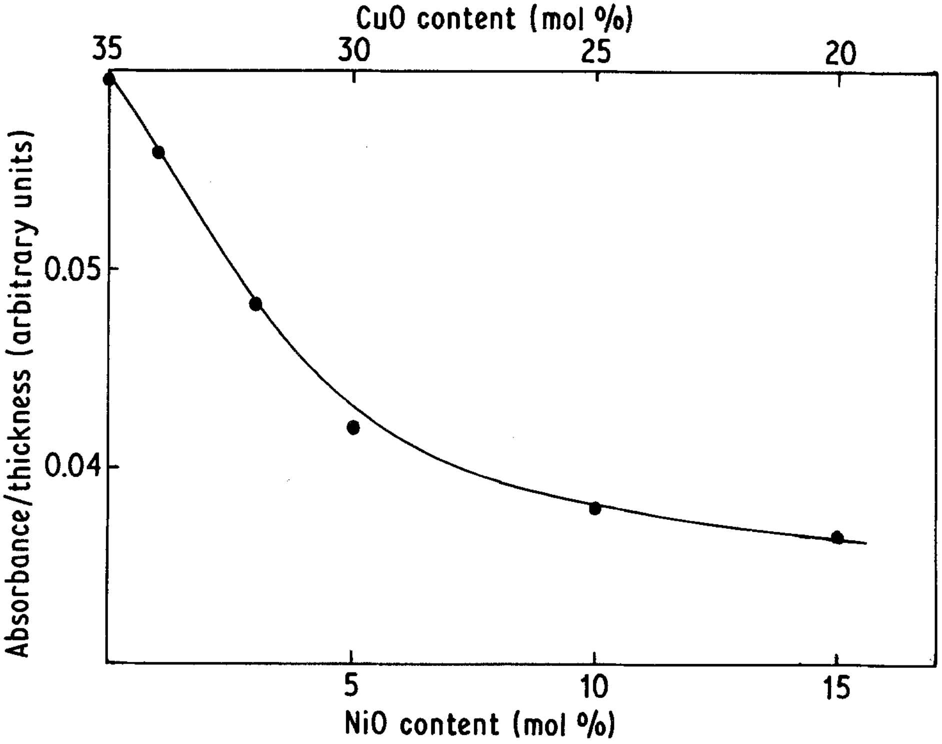

Figure 8 Absorbance due to Cu^{2+} ions in copper–nickel–phosphate glasses as a function of NiO and CuO contents.

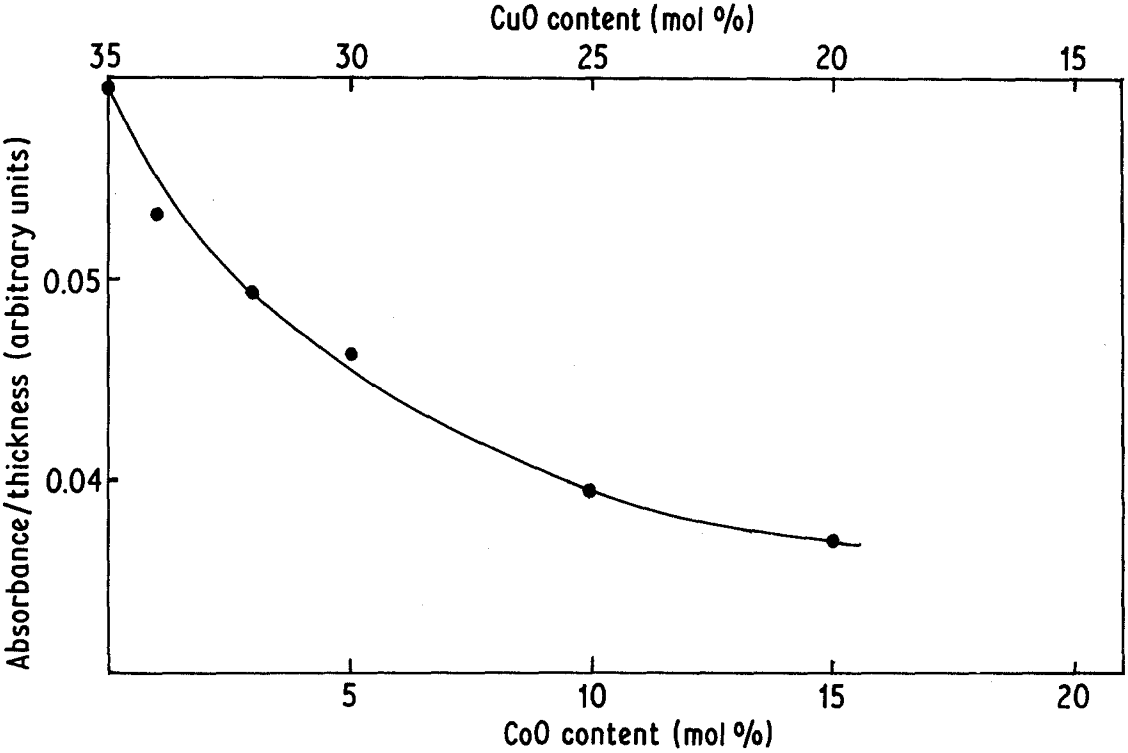

Figure 9 Absorbance due to Cu^{2+} ions in copper–cobalt–phosphate glasses as a function of CoO and CuO contents.

4. Discussion of results

Previous workers have explained the loss of ESR signal in a mixed oxide system containing copper, by a cross-relaxation process in the case of added Co^{2+} where the presence of rapidly relaxing Co^{2+} leads to a loss of Cu^{2+} signal, rather than a shift in the equilibrium $Cu^{2+} + e^- \rightleftharpoons Cu^+$ towards a diamagnetic state as observed by Abdrakhmanov *et al.* [18] and by Bogomolova *et al.* [9]. Konstants and Vaivada [19] also suggested that if there are two elements in the system which form ions of variable valency, then interaction between them usually takes place as follows:

$$Mn^{3+} + Ce^{3+} \rightleftharpoons Mn^{2+} + Ce^{4+}.$$

In both systems studied by us, enhanced chemical reduction of the cupric ion might be achieved by interaction with a reduced ion of the added transition metal, namely Ni^+ or Co^+, which together with its corresponding ion in the +2 oxidation state forms a strongly reducing couple. Ni^{2+}, unlike Co^{2+}, has a long relaxation time and therefore is unlikely to cause the loss of Cu^{2+} signal by the mechanism of cross-relaxation invoked by Bogomolova for a Co^{2+}-doped system.

The plots of the reduction of $[Cu^{2+}]$ as measured by ESR (Figs. 5 and 6) and by absorption spectroscopy (Figs. 8 and 9) show very similar trends. So from ESR and optical data it is concluded that the loss of Cu^{2+} signal in phosphate glasses containing CuO and NiO and also CuO and CoO is due to an oxidation–reduction mechanism between two valency states of the two different transition elements of the following type

$$Cu^{2+} + Ni^+ \rightleftharpoons Cu^+ + Ni^{2+}$$
$$Cu^{2+} + Co^+ \rightleftharpoons Cu^+ + Co^{2+}.$$

The absorption band at about 440 nm is observed in CuO–NiO–P_2O_5 glasses and this is due to six-coordinated Ni^{2+} ions in octahedral coordination in phosphate glasses and the absorption bands at 535, 590 and 623 nm are attributed to six-coordinated Co^{2+} ions in a tetrahedral field as described by Haddon [14] and Weyl [13]. The absorption band at 830 nm is observed and is due to Cu^{2+} ions in an octahedral field with strong tetrahedral distortion as Bates [12] described for copper in sodium silicate glasses and by Moridi and Hogarth [7] for copper phosphate glasses.

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