

# Effect of cobalt ions on the EPR and d.c. conductivity in vanadyl doped $\text{CoO-M}_2\text{O-B}_2\text{O}_3$ (M=Li, K) glasses

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Glasses having the composition  $x\text{CoO} \cdot (0.30-x)\text{M}_2\text{O} \cdot 0.70\text{B}_2\text{O}_3$  (M=Li, K) have been prepared over the range  $0.00 \leq x \leq 0.15$  containing 1.0 and 2.0 mol% of  $\text{V}_2\text{O}_5$ . Spin-Hamiltonian parameters, dipolar hyperfine coupling parameter,  $P$ , and Fermi contact interaction term,  $K$ , of the  $\text{VO}^{2+}$  ions have been calculated. It is found the  $\text{V}^{4+}$  ions in these glasses exist as  $\text{VO}^{2+}$  in octahedral coordination with a tetragonal distortion. Results suggest that hyperfine spectra on vanadium are not observed when the amount of  $\text{CoO}$  exceeds a certain value, which depends on the type of alkali and the amount of  $\text{V}_2\text{O}_5$ . The  $3d_{xy}$  orbital in the vanadium ion expands and the tetragonal distortion around vanadium ion increases with the increase in the  $\text{CoO} \cdot \text{M}_2\text{O}$  ratio. There is virtually no change in the microscopic structure around vanadium due to annealing or when  $\text{Li}_2\text{O}$  is replaced by  $\text{K}_2\text{O}$ . The d.c. conductivity decreases when  $\text{Li}_2\text{O}$  is replaced by  $\text{K}_2\text{O}$ , keeping the concentration of  $\text{CoO}$  and  $\text{B}_2\text{O}_3$  constant. Addition of  $\text{CoO}$  to the sample shows a "blocking effect" on the overall mobility of alkali ions. As a result the conductivity of the sample decreases with increase in  $\text{CoO} \cdot \text{M}_2\text{O}$  ratio.

## Introduction

Many authors have reported<sup>(1-9)</sup> detailed information regarding structural phenomena and to identify the site symmetry of sites around the transition metal (TM) ion in glasses by using electron paramagnetic resonance (EPR) spectroscopy as an experimental technique.<sup>(1-5)</sup> However, a very small number of papers have been devoted to borate glasses with mixed TM ions.

It is well known<sup>(9)</sup> that in the first row of transition elements the  $\text{Co}^{2+}$  ion relaxes fast and its electron paramagnetic resonance (EPR) lines are too broad to be observed at temperature greater than 77 K. The EPR spectra of  $\text{Co}^{2+}$  ions in oxide glasses could only be detected at 4.2 K. It has also been noted<sup>(6)</sup> that when  $\text{Co}^{2+}$  is introduced into oxide glasses containing  $\pi$  ions (where  $\pi = \text{Cu}^{2+}$ ,  $\text{VO}^{2+}$ ,  $\text{Mn}^{2+}$  and  $\text{W}^{5+}$ ) the EPR spectra of these ions attenuates. In earlier studies,<sup>(10-12)</sup> it was found that in ternary borate glasses ( $\text{Li}_2\text{O-CdO-B}_2\text{O}_3$  and  $\text{Li}_2\text{O-BaO-B}_2\text{O}_3$ ) containing 2.0 mol% of  $\text{V}_2\text{O}_5$ , variation in the  $\text{Li}_2\text{O}:\text{CdO}$  or  $\text{Li}_2\text{O}:\text{BaO}$  ratio for constant  $\text{B}_2\text{O}_3$  has no effect on the vanadium site. In these glasses  $\text{Li}_2\text{O}$ ,  $\text{BaO}$  and  $\text{CdO}$  are diamagnetic. However, the octahedral site symmetry on the  $\text{V}^{4+}$  site is improved<sup>(11)</sup> when a diamagnetic modifier,  $\text{Ba}^{2+}$ , is replaced by the paramagnetic ion,  $\text{Co}^{2+}$ , keeping  $\text{B}_2\text{O}_3$  constant in  $\text{CoO-BaO-B}_2\text{O}_3$  glasses containing

2.0 mol% of  $\text{V}_2\text{O}_5$ .

It was, therefore, of interest to study the effect of  $\text{Co}^{2+}$  ions on the features of EPR spectra of  $\text{VO}^{2+}$  doped in other oxide glasses. Structural studies of alkali borate glasses presently attract a significant interest because of their ionic conductivity and potential usages as solid electrolytes in various electro-chemical devices such as solid state batteries, fuel cells and chemical sensors.<sup>(13-15)</sup> Alkali and alkaline earth cations incorporated in the structure of glasses are responsible for ionic conduction in the materials.<sup>(16-17)</sup> Study of d.c. conductivity is also interesting because vanadium ions can exist as  $\text{V}^{4+}$  and  $\text{V}^{5+}$  species depending by the matrix composition and the preparation conditions.

In the present paper reports EPR and d.c. conductivity of the  $x\text{CoO} \cdot (0.30-x)\text{M}_2\text{O} \cdot 0.70\text{B}_2\text{O}_3$  (M=Li or K) ( $0.0 \leq x \leq 0.15$ ) doped with 1.0 and 2.0 mol% of  $\text{V}_2\text{O}_5$ .

## Glass preparation

The starting materials used to prepare the glasses were the Analar grade reagents of  $\text{Li}_2\text{CO}_3$ ,  $\text{K}_2\text{CO}_3$ ,  $\text{CoCO}_3$ ,  $\text{H}_3\text{BO}_3$  and  $\text{V}_2\text{O}_5$  which were mixed in appropriate proportions. To each batch 1.0 and 2.0 mol% of  $\text{V}_2\text{O}_5$  was added. Melting was done in porcelain crucibles at approximately 1273 K in an electrical muffle for 1 h. When all bubbles disappeared, the melts were quickly poured onto a carbon plate and

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pressed with another plate. To free the glass from internal stress a part of each sample was annealed at 473 K for 2 h.

### Experimental

#### 1. Electron Paramagnetic Resonance

First derivative EPR spectra of annealed and unannealed of the crushed samples were recorded at room temperature (300 K) in the X-band frequency on EPR spectrometers Varian E-112 as discussed in earlier paper.<sup>(12)</sup>

#### 2. D.C. conductivity

To measure the d.c. conductivity glasses in the form of slices of nearly 1 mm uniform thickness were chosen. Colloidal silver paint was used as an electrode material. D.C. conductivity was measured with the help of Keithley programmable electrometer/source. A constant voltage of 20 V was applied across the sample.<sup>(12)</sup> Measurements were made at different temperatures between 373 K and 533 K, first by increasing, and then by decreasing the temperature.

### Results

#### 1. EPR

Figures 1 and 2 illustrate hyperfine spectra of VO<sup>2+</sup> ion in unannealed CoO-M<sub>2</sub>O-B<sub>2</sub>O<sub>3</sub> (M=Li or K) samples at 300 K. There is no change in the EPR spectra on annealing. The spectra have structures which are characteristic of a hyperfine interaction arising from an unpaired electron with the <sup>51</sup>V nucleus whose spin is 7/2 and which is present in 99.75% abundance.<sup>(18)</sup> These spectra were analysed by assuming<sup>(5,10,19)</sup> that vanadium is present as a vanadyl ion in a ligand field of C<sub>4v</sub> symmetry.

The spin Hamiltonian used is of the form<sup>(20)</sup>

$$H = \beta g_{\parallel} B_z S_z + \beta g_{\perp} (B_x S_x + B_y S_y) + A_{\parallel} S_z I_z + A_{\perp} (S_x I_x + S_y I_y) \quad (1)$$

where the symbols have their usual meaning. Quadrupole and nuclear Zeeman interaction terms are ignored. The solutions<sup>(21)</sup> of the spin-Hamiltonian<sup>(1)</sup> are given in Equations (2) and (3) for the parallel and perpendicular orientation, respectively

$$B_{\parallel}(m) = B_{\parallel}(0) - mA_{\parallel} - \{63/4 - m^2\} A_{\perp}^2 / 2B_{\parallel}(0) \quad (2)$$

$$B_{\perp}(m) = B_{\perp}(0) - mA_{\perp} - \{63/4 - m^2\} (A_{\parallel}^2 + A_{\perp}^2) / 4B_{\perp}(0) \quad (3)$$

where *m* is the magnetic quantum number of the vanadium nucleus having values ±7/2, ±5/2, ±3/2 and ±1/2

$$B_{\parallel}(0) = h\nu / g_{\parallel} \beta \quad \text{and} \quad B_{\perp}(0) = h\nu / g_{\perp} \beta$$

with *h* as the Planck constant, *ν* as the frequency of the spectrometer and β as the Bohr magneton. Measurements for the B<sub>∥</sub> position were taken which correspond to a maximum in the first derivative curve

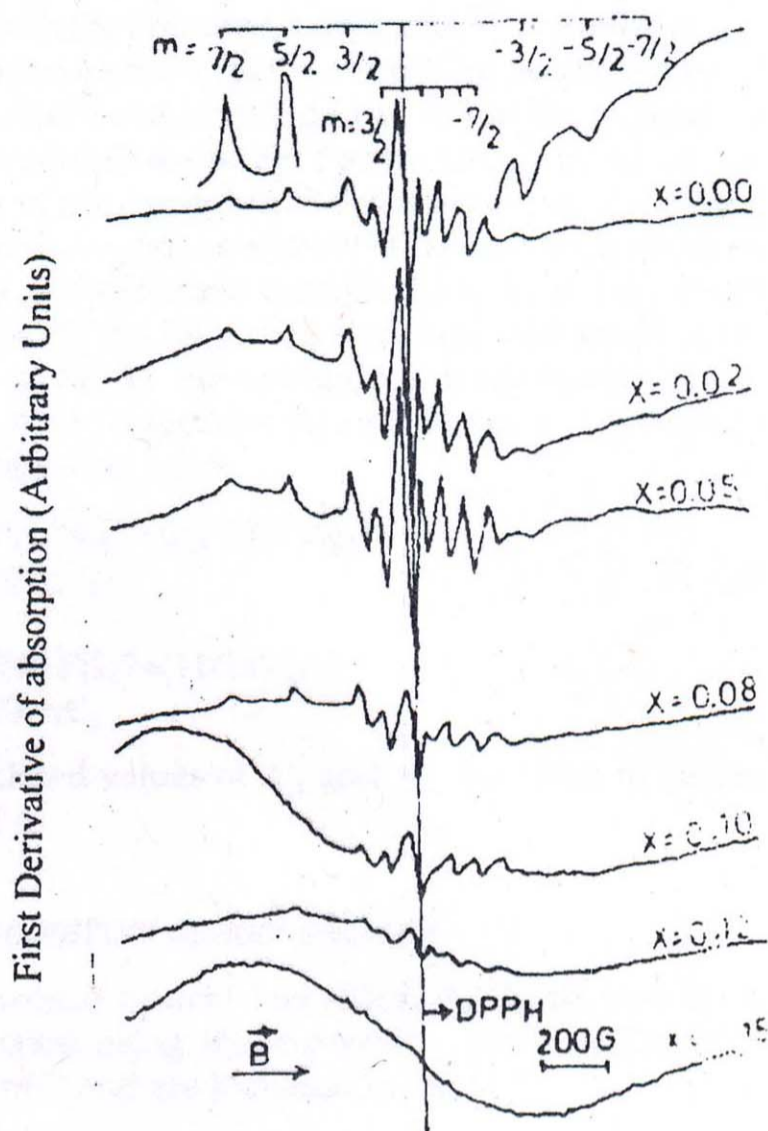


Figure 1. The EPR spectra of VO<sup>2+</sup> ions in xCoO-(0.30-x)Li<sub>2</sub>O-0.70 B<sub>2</sub>O<sub>3</sub> (0.00 ≤ x ≤ 0.15) glasses containing 2.0 mol% of V<sub>2</sub>O<sub>5</sub> in the X-band (ν ~ 9.3 GHz) at 300 K

of the parallel hfs component for a given *m* value, whereas the B<sub>⊥</sub> position is enclosed between the first derivative perpendicular peak and its "zero".<sup>(20)</sup> Spin-Hamiltonian parameters of VO<sup>2+</sup> ion determined from the observed positions of spectral lines and using Equations (2) and (3) are given in Tables 1 and 2. From the values of these parameters the dipolar hyperfine coupling parameter,  $P = 2\gamma\beta_e\beta_N\langle r^{-3} \rangle$  and the Fermi contact interaction term, *K*, are evaluated by using

Table 1. Spin Hamiltonian parameters<sup>a</sup> and Λ<sub>th</sub> of VO<sup>2+</sup> in unannealed xCoO-(0.3-x) Li<sub>2</sub>O-0.7B<sub>2</sub>O<sub>3</sub> glasses at room temperature

Glass No.	x	V <sub>2</sub> O <sub>5</sub> (mol%)	g <sub>∥</sub> (±0.001)	g <sub>⊥</sub> (±0.001)	A <sub>∥</sub>   (10 <sup>-4</sup> cm <sup>-1</sup> ) (±1.0)	A <sub>⊥</sub>   (10 <sup>-4</sup> cm <sup>-1</sup> ) (±1.0)	Λ <sub>th</sub>
L1	0.00	1.0	1.9421	1.9741	170.1	58.8	0.4940
L2	0.02	1.0	1.9422	1.9743	170.1	58.6	0.4897
L3	0.04	1.0	1.9414	1.9744	170.1	59.2	0.4854
L4	0.05	1.0	1.9415	1.9752	169.9	59.2	0.4831
L5	0.06	1.0	1.9404	1.9760	169.9	60.0	0.4809
L6	0.08	1.0	-	-	-	-	0.4767
L7	0.00	2.0	1.9412	1.9721	169.5	58.8	0.4940
L8	0.02	2.0	1.9413	1.9745	169.6	59.2	0.4897
L9	0.05	2.0	1.9401	1.9752	169.7	59.2	0.4831
L10	0.08	2.0	1.9404	1.9752	169.8	59.2	0.4767
L11	0.10	2.0	1.9404	1.9764	169.8	59.7	0.4724
L12	0.12	2.0	-	-	-	-	0.4681
L13	0.15	2.0	-	-	-	-	0.4616

<sup>a</sup> A<sub>∥</sub> and A<sub>⊥</sub> are negative

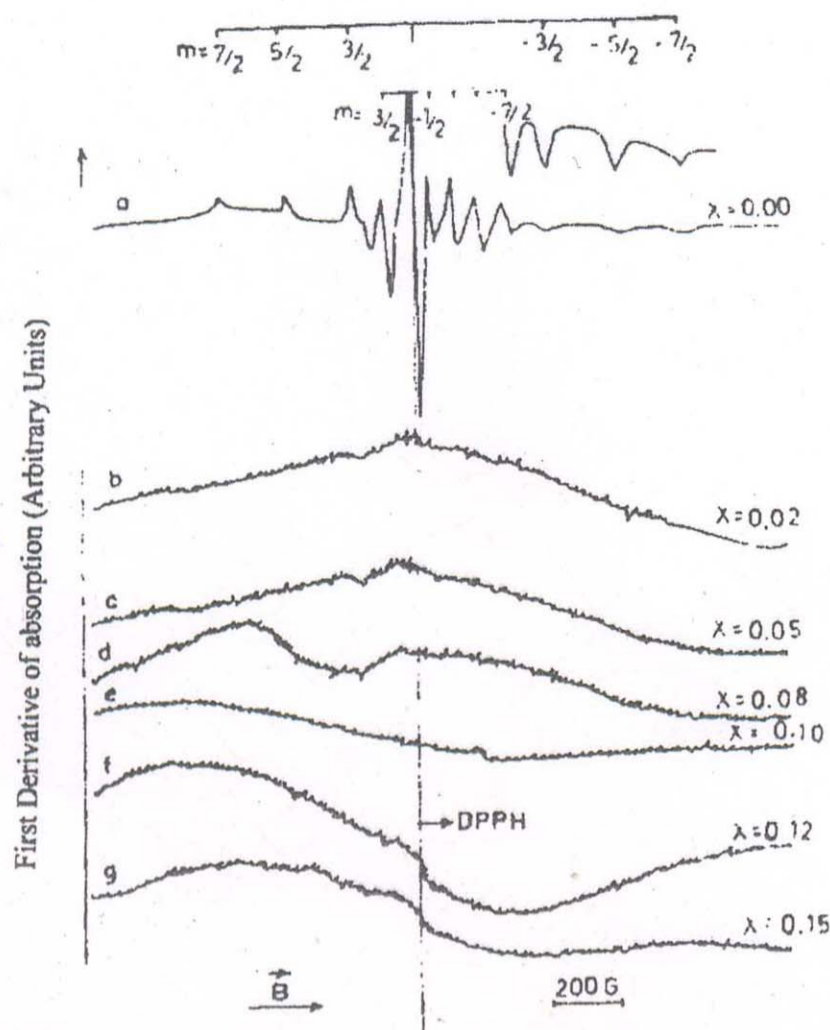


Figure 2. The EPR spectra of  $VO^{2+}$  ions in  $xCoO-(0.30-x)K_2O-0.70B_2O_3$  ( $0.00 \leq x \leq 0.15$ ) glasses containing 2.0 mol% of  $V_2O_5$  in the X-band ( $\nu \sim 9.3$  GHz) at 300 K

the expressions developed by Kivelson & Lee<sup>(22)</sup>

$$A_{\parallel} = P[K + 4/7 - \Delta g_{\parallel} - (3/7)\Delta g_{\perp}] \quad (4)$$

$$A_{\perp} = P[K - 2/7 - (11/14)\Delta g_{\perp}] \quad (5)$$

where  $\Delta g_{\parallel} = g_{\parallel} - g_e$ ;  $\Delta g_{\perp} = g_{\perp} - g_e$  and  $g_e (= 2.0023)$  is the  $g$  factor of free electrons. Both  $A_{\parallel}$  and  $A_{\perp}$  are found to be negative by the method proposed by Muncaster & Parke.<sup>(18)</sup> The term  $-PK$  in Equations (4) and (5) is due to  $s$ -character of the magnetic spin of the vanadium. This  $s$ -character arises due to partial unpairing or polarisation of the  $s$  electrons as a result of an interac-

Table 2. Spin Hamiltonian parameters<sup>a</sup> and  $\Lambda_{th}$  of  $VO^{2+}$  in unannealed  $xCoO-(0.3-x)K_2O-0.7B_2O_3$  glasses at room temperature

Glass No.	x	$V_2O_5$ (mol%)	$g_{\parallel}$ ( $\pm 0.001$ )	$g_{\perp}$ ( $\pm 0.001$ )	$ A_{\parallel} $ ( $10^{-4} cm^{-1}$ ) ( $\pm 1.0$ )	$ A_{\perp} $ ( $10^{-4} cm^{-1}$ ) ( $\pm 1.0$ )	$\Lambda_{th}$
K1	0.00	1.0	1.9422	1.9751	168.9	59.0	0.5394
K2	0.02	1.0	-	-	-	-	0.5325
K3	0.04	1.0	-	-	-	-	0.5256
K4	0.05	1.0	-	-	-	-	0.5214
K5	0.06	1.0	-	-	-	-	0.5176
K6	0.08	1.0	-	-	-	-	0.5104
K7	0.00	2.0	1.9422	1.9734	168.5	57.9	0.5394
K8	0.02	2.0	-	-	-	-	0.5325
K9	0.05	2.0	-	-	-	-	0.5214
K10	0.08	2.0	-	-	-	-	0.5031
K11	0.10	2.0	-	-	-	-	0.4957
K12	0.12	2.0	-	-	-	-	0.4846
K13	0.15	2.0	-	-	-	-	-

<sup>a</sup>  $A_{\parallel}$  and  $A_{\perp}$  are negative

tion with the unpaired  $d$  electrons.<sup>(23)</sup> The effect of polarisation on the hyperfine coupling was determined by Heine<sup>(23)</sup> and is included as  $-PK$  in the expression for hyperfine coupling. For transition metal ions  $K$  is found to be positive.<sup>(24)</sup> From the molecular orbital theory it can also be shown<sup>(7)</sup> that the components  $A_{\parallel}$  and  $A_{\perp}$  consist of the contributions  $A'_{\parallel}$  and  $A'_{\perp}$  of the electron to the hyperfine structure and the  $PK$  term arising due to the anomalous contribution of the  $s$ -electrons. Equations (4) and (5) can be rewritten in the following form

$$A_{\parallel} = -PK - P[4/7 - \Delta g_{\parallel} - (3/7)\Delta g_{\perp}] = -PK + A'_{\parallel} \quad (6)$$

$$A_{\perp} = -PK + P[2/7 + (11/14)\Delta g_{\perp}] = -PK + A'_{\perp} \quad (7)$$

Calculated values of  $A'_{\parallel}$  and  $A'_{\perp}$  are given in Tables 3 and 4.

## 2. Theoretical optical basicity

Theoretical optical basicities,  $\Lambda_{th}$  have also been calculated using the expression given by Duffy & Ingram<sup>(25)</sup> and are included in Table 1.

## 3. D.C. conductivity

Figures 3(a) and (b) and 4(a) and (b) show the variation of  $\log \sigma$  ( $\sigma$  is the electrical conductivity) against  $1000/T$  for these glasses. In general the conductivity increases with the temperature and the variation of the conductivity of the samples over an accessible temperature range of about 100 K is about two orders of magnitude in all these glasses. From these figures it clear that  $\log \sigma$  against  $1000/T$  plots are linear for temperature higher than 400 K. These linear curves satisfy the relation

$$\sigma = \sigma_0 \exp(-W/kT) \quad (10)$$

where  $\sigma_0$  is a constant for a given glass,  $k$  is the Boltzmann constant and  $W$  is the activation energy

Table 3.  $P$ ,  $K$ ,  $|A'_{\parallel}|$ ,  $|A'_{\perp}|$  and  $\Delta g_{\parallel}/\Delta g_{\perp}$  of  $VO^{2+}$  in unannealed  $xCoO-(0.3-x)Li_2O-0.7B_2O_3$  glasses at room temperature

Glass No.	$P$ ( $10^{-4} cm^{-1}$ )	$K$	$ A'_{\parallel} $ ( $10^{-4} cm^{-1}$ )	$ A'_{\perp} $ ( $10^{-4} cm^{-1}$ )	$\Delta g_{\parallel}/\Delta g_{\perp}$
L1	122.7	0.743	79.0	32.3	2.1491
L2	122.7	0.741	79.0	32.3	2.1532
L3	122.2	0.748	78.7	32.2	2.1860
L4	121.7	0.751	78.5	32.2	2.2492
L5	120.8	0.762	77.9	32.0	2.3383
L6	-	-	-	-	-
L7	122.9	0.745	78.7	32.0	2.0472
L8	121.6	0.750	78.4	32.0	2.1471
L9	121.3	0.752	78.4	32.0	2.2552
L10	121.4	0.752	78.4	32.1	2.3161
L11	120.9	0.761	78.9	32.0	2.3513
L12-L13	-	-	-	-	-

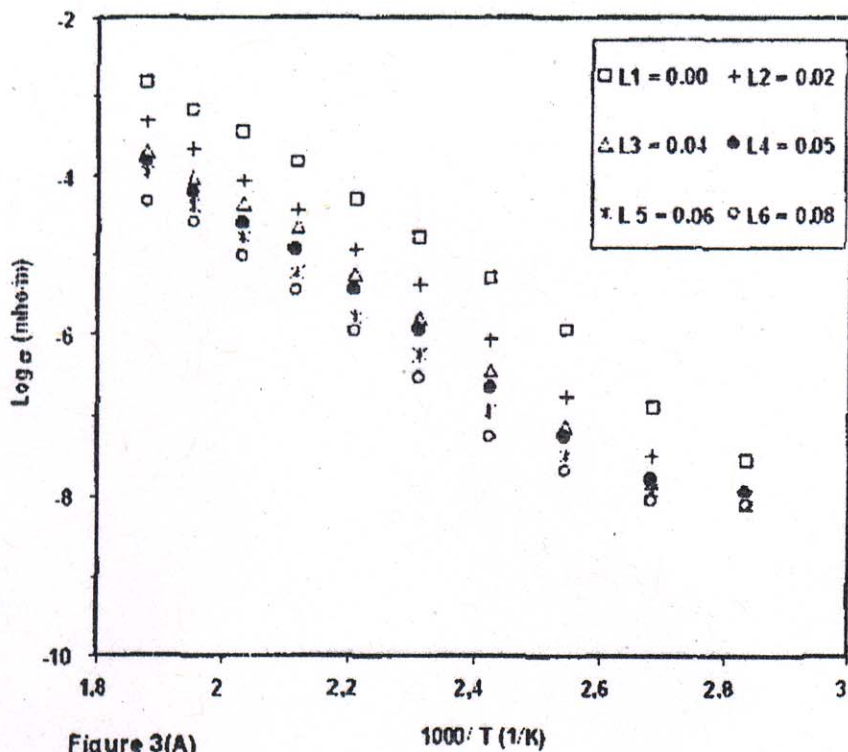


Figure 3(A). Variation of  $\log \sigma$  as a function of  $1000/T$  for  $x\text{CoO}-(0.30-x)\text{Li}_2\text{O}-0.70\text{B}_2\text{O}_3$  ( $0.00 \leq x \leq 0.08$ ) glasses containing 1.0 mol% of  $\text{V}_2\text{O}_5$

for conduction. The activation energy,  $W$  and pre-exponential term,  $\sigma_\infty$  were determined by using the least square fitting of the experimental data with the relation

$$\log \sigma = \log \sigma_\infty - (W/1000k)(1000/T) \quad (11)$$

The calculated values of activation energy, pre-exponential term and measured value of conductivity are given in Tables 5 and 6.

## Discussion

### 1. EPR

The value of  $\Delta g_{\parallel}/\Delta g_{\perp}$ , which measures the tetragonality of the vanadium site<sup>(7)</sup> is also included in Tables 3, 4. EPR spectra (Figures 1 and 2) reveal that the hyperfine spectra of  $\text{VO}^{2+}$  ion in  $\text{CoO}-\text{Li}_2\text{O}-\text{B}_2\text{O}_3$  samples is not observed when 1.0 mol% of  $\text{V}_2\text{O}_5$  along with  $\geq 8.0$  mol% of  $\text{CoCO}_3$  is added in the samples (whereas the hyperfine spectra of  $\text{VO}^{2+}$  ion in these samples is not observed when 2.0 mol% of  $\text{V}_2\text{O}_5$  with more than 12.0 mol% of  $\text{CoCO}_3$  are added

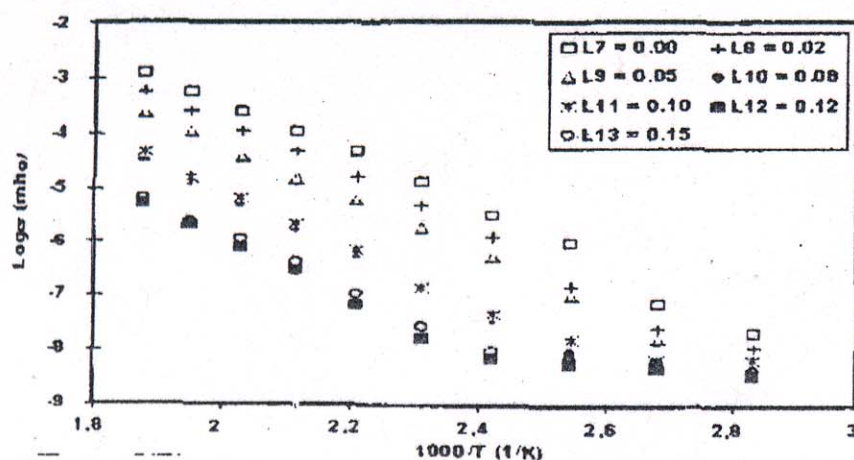


Figure 3(b). Variation of  $\log \sigma$  as a function of  $1000/T$  for  $x\text{CoO}-(0.30-x)\text{Li}_2\text{O}-0.70\text{B}_2\text{O}_3$  ( $0.00 \leq x \leq 0.15$ ) glasses containing 2.0 mol% of  $\text{V}_2\text{O}_5$

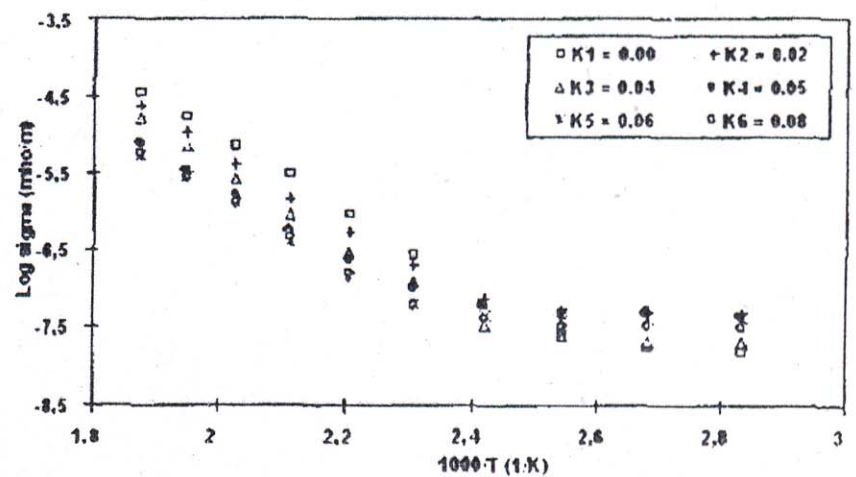


Figure 4(a). Variation of  $\log \sigma$  as a function of  $1000/T$  for  $x\text{CoO}-(0.30-x)\text{K}_2\text{O}-0.70\text{B}_2\text{O}_3$  ( $0.00 \leq x \leq 0.08$ ) glasses containing 1.0 mol% of  $\text{V}_2\text{O}_5$

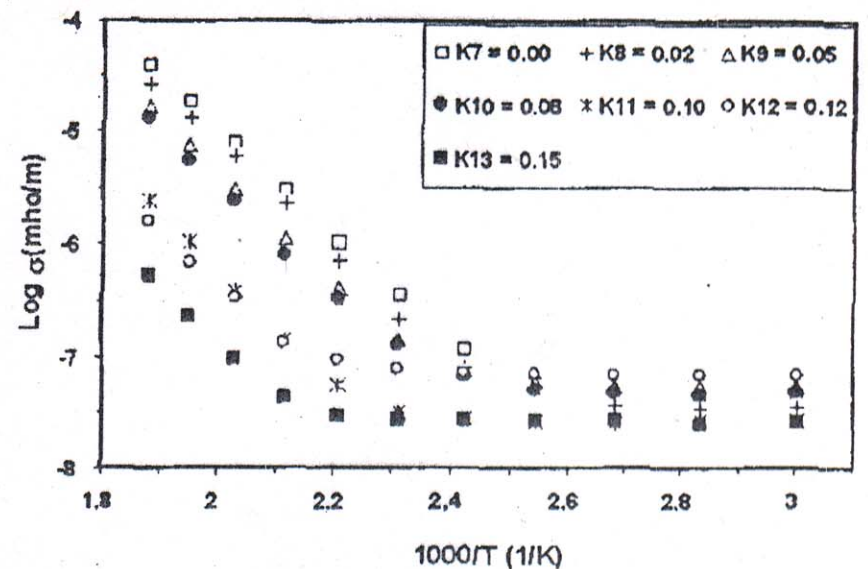


Figure 4(b). Variation of  $\log \sigma$  as a function of  $1000/T$  for  $x\text{CoO}-(0.30-x)\text{K}_2\text{O}-0.70\text{B}_2\text{O}_3$  ( $0.00 \leq x \leq 0.15$ ) glasses containing 2.0 mol% of  $\text{V}_2\text{O}_5$

in the samples). In  $\text{CoO}-\text{K}_2\text{O}-\text{B}_2\text{O}_3$  samples with 1.0 mol% or 2.0 mol% of  $\text{V}_2\text{O}_5$  the hyperfine spectra is not observed even when only 2.0 mol% of  $\text{CoCO}_3$  is added in the sample. The  $\text{V}^{4+}$  ions presences are not influenced not only by the cobalt ones but also by the other components. At so small  $\text{V}_2\text{O}_5$  content of vanadium must be present in  $\text{V}^{4+}$  and  $\text{V}^{5+}$  ions but as  $\text{V}^{5+}$  is diamagnetic so its contribution towards EPR spectra is absent. Absence of the hyperfine spectra may be due to the absence of  $\text{V}^{4+}$  ions or presence of cobalt ions as discussed below.

Following hypothesis may be given to try to explain the absence of hyperfine spectra in these samples.  $\text{Co}^{2+}$  has very short spin lattice relaxation time, as a result its EPR in borate glasses is not observed down to liquid nitrogen temperature.<sup>(26)</sup> On the other hand,

Table. 4  $P$ ,  $K$ ,  $|A'_{\parallel}|$ ,  $|A'_{\perp}|$  and  $\Delta g_{\parallel}/\Delta g_{\perp}$  of  $\text{VO}^{2+}$  in unannealed  $x\text{CoO}-(0.3-x)\text{K}_2\text{O}-0.7\text{B}_2\text{O}_3$  glasses at room temperature

Glass No.	$P$ ( $10^{-3} \text{ cm}^{-1}$ )	$K$	$ A'_{\parallel} $ ( $10^{-2} \text{ cm}^{-1}$ )	$ A'_{\perp} $ ( $10^{-2} \text{ cm}^{-1}$ )	$\Delta g_{\parallel}/\Delta g_{\perp}$
K1	121.2	0.751	78.0	32.0	2.1701
K2-K6	-	-	-	-	-
K7	121.2	0.738	78.5	32.0	2.0902
K8-K13	-	-	-	-	-

Table 5. D.C. conductivity,  $\sigma$  activation energy,  $W$  and pre-exponential term,  $\log \sigma_0$ , of  $x\text{CoO}-(0.3-x)\text{Li}_2\text{O}-0.70\text{B}_2\text{O}_3$  glasses

Glass No.	x	V <sub>2</sub> O <sub>5</sub> (mol%)	$\sigma_{at 433 K}$ ( $\Omega^{-1}m^{-1}$ )	$\sigma_{at 533 K}$ ( $\Omega^{-1}m^{-1}$ )	$\log \sigma_0$	W (eV)
L1	0.00	1.0	$1.7 \times 10^{-5}$	$1.5 \times 10^{-3}$	5.68	0.90
L2	0.02	1.0	$4.0 \times 10^{-6}$	$4.9 \times 10^{-4}$	6.04	0.98
L3	0.04	1.0	$1.0 \times 10^{-6}$	$2.0 \times 10^{-4}$	5.80	0.99
L4	0.05	1.0	$1.0 \times 10^{-6}$	$1.5 \times 10^{-4}$	5.73	1.01
L5	0.06	1.0	$5.8 \times 10^{-7}$	$1.1 \times 10^{-4}$	6.14	1.06
L6	0.08	1.0	$2.9 \times 10^{-7}$	$4.5 \times 10^{-5}$	5.93	1.07
L7	0.00	2.0	$1.2 \times 10^{-5}$	$1.3 \times 10^{-3}$	5.96	0.93
L8	0.02	2.0	$4.0 \times 10^{-6}$	$5.9 \times 10^{-4}$	5.99	0.97
L9	0.05	2.0	$1.0 \times 10^{-6}$	$2.4 \times 10^{-4}$	5.77	0.99
L10	0.08	2.0	$1.4 \times 10^{-7}$	$4.5 \times 10^{-5}$	5.82	1.08
L11	0.10	2.0	$1.4 \times 10^{-7}$	$4.6 \times 10^{-5}$	5.88	1.08
L12	0.12	2.0	$1.7 \times 10^{-8}$	$5.0 \times 10^{-6}$	4.91	1.08
L13	0.15	2.0	$2.8 \times 10^{-8}$	$6.0 \times 10^{-6}$	5.02	1.08

VO<sup>2+</sup> has long spin lattice relaxation time. We assume that samples containing VO<sup>2+</sup> and Co<sup>2+</sup> can be treated as two spin systems having quite different spin lattice relaxation times. According to this assumption there is a difference in the spin temperatures of these systems. When there is thermal contact between these system (realised through dipole-dipole interaction) equalisation of their temperature can take place (cross relaxation).<sup>(8)</sup> Although the overlap regions for the Co<sup>2+</sup> and VO<sup>2+</sup> spectra are insignificant but for sufficiently high Co<sup>2+</sup> concentration (12.0 mol% in case of CoO-Li<sub>2</sub>O-B<sub>2</sub>O<sub>3</sub> sample, more than 2.0 mol% in case of CoO-K<sub>2</sub>O-B<sub>2</sub>O<sub>3</sub> sample), there is sharp decrease in the spin lattice relaxation time for all VO<sup>2+</sup> ions regardless of where this ion makes its contribution to the spectrum. We can, therefore, conclude that the presence of the medium of rapidly relaxing Co<sup>2+</sup> ions leads to the rapid relaxation of adjacent VO<sup>2+</sup> ions so that the latter do not make any contribution to the net intensity of EPR signal. Thus, hyperfine spectra of VO<sup>2+</sup> in these compositions are not observed.

Tables 1 to 4 indicate that the values of  $g_{\perp}$ ,  $A_{\perp}$ ,  $K$  and  $\Delta g_{\parallel}/\Delta g_{\perp}$  increase and the values of  $A_{\parallel}$ ,  $P$ ,  $|A'_{\parallel}|$  and  $|A'_{\perp}|$  decrease when M<sub>2</sub>O is replaced by CoO. As suggested by Kivelson & Lee,<sup>(22)</sup> we assume the increased in the values of  $K$  with increase in the CoO:M<sub>2</sub>O ratio as due<sup>(27-30)</sup> to an increase in the tetragonal nature of the V<sup>4+</sup>O<sub>6</sub> complex because of a strongly bonded oxygen atom at the V<sup>4+</sup> ion in the site opposite to the vanadyl oxygen. The increase in  $\Delta g_{\parallel}/\Delta g_{\perp}$  also shows that the octahedral symmetry is reduced when M<sub>2</sub>O is replaced by CoO. The decrease of the anisotropic contribution (i.e.  $|A'_{\parallel}|$  and  $|A'_{\perp}|$ ) of the 3dxy electron to the hyperfine splitting is brought about by increasing<sup>(7)</sup> screening of the 3dxy orbital from its nucleus through overlap of the electron orbits of the surrounding oxygen ligands. This screening produces an expansion of the 3dxy orbital, resulting in a decreased interaction between this magnetic electron with the vanadium nucleus. The decreasing value of  $P$  also supports the argument that 3dxy orbit

 Table 6. D.C. conductivity,  $\sigma$  activation energy,  $W$  and pre-exponential term,  $\log \sigma_0$ , of  $x\text{CoO}-(0.3-x)\text{K}_2\text{O}-0.70\text{B}_2\text{O}_3$  glasses

Glass No.	x	V <sub>2</sub> O <sub>5</sub> (mol%)	$\sigma_{at 433 K}$ ( $\Omega^{-1}m^{-1}$ )	$\sigma_{at 533 K}$ ( $\Omega^{-1}m^{-1}$ )	$\log \sigma_0$	W (eV)
K1	0.00	1.0	$2.7 \times 10^{-7}$	$3.5 \times 10^{-5}$	4.71	0.96
K2	0.02	1.0	$2.0 \times 10^{-7}$	$2.3 \times 10^{-5}$	4.47	0.96
K3	0.04	1.0	$1.2 \times 10^{-7}$	$1.6 \times 10^{-5}$	4.46	0.98
K4	0.05	1.0	$1.0 \times 10^{-6}$	$7.0 \times 10^{-6}$	3.92	0.95
K5	0.06	1.0	$6.2 \times 10^{-8}$	$5.0 \times 10^{-6}$	3.89	0.96
K6	0.08	1.0	$6.0 \times 10^{-8}$	$5.0 \times 10^{-6}$	3.69	0.94
K7	0.00	2.0	$3.6 \times 10^{-7}$	$4.0 \times 10^{-5}$	4.41	0.93
K8	0.02	2.0	$2.2 \times 10^{-7}$	$2.7 \times 10^{-5}$	4.38	0.94
K9	0.05	2.0	$1.4 \times 10^{-7}$	$1.6 \times 10^{-5}$	4.20	0.95
K10	0.08	2.0	$1.3 \times 10^{-7}$	$1.3 \times 10^{-5}$	4.20	0.96
K11	0.10	2.0	$3.2 \times 10^{-8}$	$2.4 \times 10^{-6}$	3.64	0.98
K12	0.12	2.0	$7.7 \times 10^{-8}$	$1.6 \times 10^{-6}$	2.56	0.88
K13	0.15	2.0	$2.8 \times 10^{-8}$	$5.2 \times 10^{-7}$	2.30	0.91

expands with increase in CoO:M<sub>2</sub>O ratio.

## 2. Theoretical optical basicity

Theoretical optical basicity serves in the first approximation as a measure<sup>(3)</sup> of the ability of oxygen to donate a negative charge in the glass. In other words, the optical basicity reflects the Lewis basicity of oxide glasses. As the ability of the equatorial ligands to donate the electron (i.e. Lewis basicity) decreases,  $\pi$  bonding between V<sup>4+</sup> and the ligands reduces.<sup>(4)</sup> This reduction, in turn increases the positive charge on V<sup>4+</sup> and increases the  $\pi$  bonding between V<sup>4+</sup> and vanadyl oxygen. This increase, decreases bond length of V<sup>4+</sup> (vanadyl oxygen). Consequently, the tetragonal nature of the V<sup>4+</sup>O<sub>6</sub> complex is enhanced. In the present system, the theoretical optical basicity,  $\Lambda_{th}$  of the host glass decreases when M<sub>2</sub>O is replaced by CoO.

## 3. D.C. conductivity

From Tables 5 and 6 following observations can be made:

- (1) The d.c. conductivity increases with increase in temperature.
- (2) The d.c. conductivity decreases when M<sub>2</sub>O (M=Li or K) is replaced by CoO.
- (3) The d.c. conductivity decreases when Li<sub>2</sub>O is replaced by or K<sub>2</sub>O keeping mol% of CoO and B<sub>2</sub>O<sub>3</sub> constants.
- (4) The d.c. conductivity increases when V<sub>2</sub>O<sub>5</sub> is changed from 1.0 mol% to 2.0 mol% in cobalt alkali borate glasses.

Similar results have been reported by others.<sup>(31-35)</sup> Figures 3(a) and (b) and 4(a) and (b) depict that  $\log$  Conductivity of CoO-M<sub>2</sub>O-B<sub>2</sub>O<sub>3</sub> samples from 310 K to 410 K ( $1000/T \geq 2.4$ ) is almost constant. It is reported by Angel *et al.*<sup>(35)</sup> in potassium silicate glass that for alkali concentration greater than 7.0 mol% occupation of available nearest neighbour sites begins to increase. In order for an alkali jump to a new site, a

nearest neighbour alkali atom may also have to jump to open an adjacent site. Because of the high site occupancy, the probability of an alkali jumping back to its original site is also much higher. In the present system  $M_2O$  is equal to 15.0 mol%. As a result at temperature below 400 K the probability of an alkali ion jumping back to its original site may be more than the probability of its jumping to its adjacent site and observed variation of conductivity in this region is very small. The decrease in d.c. conductivity by replacing  $Li_2O$  with  $K_2O$  suggests that conductivity has contribution from ionic conductivity because  $K^+$  ion is a heavy particle as compared to  $Li^+$ . The d.c. conductivity of lithium glass is maximum due to the fact  $Li^+$  ions are lightest as compared to  $K^+$  ions. As Vanadium ions can be present in more than one valence states, i.e.  $V^{4+}$  and  $V^{5+}$ , conduction could also take place by transfer of electrons from low to high valence states. Decrease in conductivity with time reveals that the electrical conductivity is mainly due to alkali ions and it may have only negligible contribution of electronic conductivity.  $S_{ov}$  Electronic conductivity due to hopping of electrons between  $V^{4+}$  and  $V^{5+}$  does not play an important role in total conductivity in the present glass system.

Decrease in d.c. conductivity and increase in activation energy by increasing the ratio of  $CoO:M_2O$  ( $M=Li$  or  $K$ ) indicate that  $CoO$  in the sample shows "blocking effect" by cobalt ions on the overall mobility of alkali ions. A similar argument was considered by Khawaja *et al*<sup>(34)</sup> for the decrease in the conductivity of sodium germanate glass when copper is added to it.

## Conclusions

From the present study of EPR and d.c. conductivity in alkali borate glasses, the following conclusions can be made:

- (1) Hyperfine spectra of vanadium are not observed when the amount of  $CoO$  exceeds certain values which depends on the type of alkali and amount of  $V_2O_5$ .
- (2) By keeping  $B_2O_3$  constant in  $CoO-M_2O-B_2O_3$  ( $M=Li$  or  $K$ ) samples, the increase in  $CoO:M_2O$  ratio may result in an increase in the tetragonal nature of the  $V^{4+}O_6$  complex.
- (3) Increase in the  $CoO:M_2O$  ratio may result in the expansion of  $3d_{xy}$  orbit of the unpaired electron in the vanadium ion in  $CoO-M_2O-B_2O_3$ .
- (4) There is virtually no change in the microscopic structure around the vanadium ion due to annealing in  $CoO-M_2O-B_2O_3$  ( $M=Li$  or  $K$ ) samples. There is virtually no change in the microscopic structure around the vanadium ion when  $Li_2O$  is replaced by  $K_2O$  in the  $0.3Li_2O \cdot 0.7B_2O_3$  sample.
- (5) The theoretical optical basicity of the  $CoO-M_2O-$

$B_2O_3$  samples decreases when  $CoO$  is substituted for  $M_2O$  predicting that the tetragonal distortion of  $V^{4+}O_6$  should increase with increase in the concentration of  $CoO$ . It also predicts that the bond length of  $V^{4+}$  and vanadyl oxygen should increase with increase in mol% of  $CoO$ . These predictions are consistent with the experimental findings.

- (6) In  $CoO-M_2O-B_2O_3$  glasses, the d.c. conductivity increase with increase in temperature.
- (7) Electrical conductivity decreases when  $Li_2O$  is replaced by  $K_2O$ , keeping the concentration of  $CoO$  and  $B_2O_3$  constant.
- (8) Addition of  $CoO$  in the sample shows a "blocking effect" on the overall mobility of alkali ions. As a result the conductivity of the sample decreases with increase in  $CoO:M_2O$  ratio.

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